INVESTIGATING ADSORPTION CHARACTERISTICS OF *Delonix regia* FOR HEAVY METALS REMOVAL IN WASTEWATER AND ITS POTENTIAL FOR REMEDIATING CONTAMINATED SOILS

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Declaration

I, Babalola Bolanle Morayo hereby confirm that the work presented in this thesis is my own and that where information was derived from other sources, they were referenced in this thesis.

Dedication

I dedicate this PhD. Thesis to God my source and strength. The One who is faithful to His word, May His name be praised forever.

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Abstract

There is need to explore all possible agro-based inexpensive adsorbents and study their feasibility for heavy metal removal with the aim of finding which is a better alternative to activated carbon. The focus of the present study is on investigating the adsorption characteristics of D*elonix regia* for the sorption of Pb, Ni, Cu, Cd and Co from polluted water and stabilization of contaminated soils. The focus also included assessment of available metal concentrations, pool size and kinetic resupply using Diffusive Gradient in Thin film (DGT) technique and DGT- Induced Fluxes in Sediments (DIFS) model.

Batch adsorption experiments were carried out using the adsorbent prepared from the pods and leaves of *Delonix regia* in order to determine the suitable operating parameters for the adsorption of the target heavy metals from synthetic metal solutions. Results showed significant uptake occurred at pH 2 which makes the adsorbent suitable for use on low pH heavy metal bearing effluents. An interaction time of 30 minutes was sufficient to achieve maximum uptake. The kinetics of adsorption best fitted to the pseudo second order kinetic model while Langmuir and Freundlich isotherms were used to interpret data obtained from initial concentration study. The experimental adsorption capacity of the pods is 31.2mgPb/g; 5.9mgNi/g; 9.1mgCu/g; 6.5mgCd/g and 5.8mgCo/g while the leaves powder has 10.3mgPb/g; 10.3mgNi/g; 9.2mgCu/g; 8.4mgCd/g and 10.3mgCo/g.

The investigation on the sorption ability of *Delonix regia* continued by using the pods on tropical soil samples to study the effect of aging; pollutants concentration difference; soil pH and soil organic matter on the removal efficiency of *Delonix regia* pods and biochar for Pb, Cu and Cd during the 42 days aging time. Results showed

that removal efficiency was dependent on aging and soil pH for both materials and all metals studied except for Cd where soil pH had no effect. *Delonix regia* could be used to remove these target metals from organic matter rich agricultural soil while the biochar with higher removal efficiency in most soil samples is better suitable for acidic and poor organic matter soils.

Further investigation for availability and resupply kinetic assessment before and after remediation was done using the DGT technique and DIFS model. The use of *Delonix.regia* and biochar resulted in a reduction in Css and C_{DGT} for all metals in the order of Biochar-treated soils < *D. regia* treated soils< control samples; an evidence of the good remediation that was achieved by each treatment. The labile pool size of metals, Kd, (Pb, Cu and Cd) that can be resupplied to soil solution from the soil solid phase follows the order of Bio-treated soils > *Delonix.regia* treated soils > control soil samples. The depletion time (Tc) and the desorption rate constant, k_{-1}, values followed the order: control samples > *Delonix.regia* treated soil > biochar treated soils. The Kd, labile pool size is increasing with aging time. In control samples, the Tc decreased with aging; while in treated soils, Tc increased with aging and *D.regia* have the higher value. In the soils to which organic matter, OM, were added, Tc values were the same for each metal throughout the aging period. The values obtained were the same for individual soil with and without treatment but vary from metal to metal. In the OM soils, treatment types and aging have no effect on metal resupply. The resupply of Pb is the fastest, then Cd and the slowest was Cu. The R values in the control soils were reducing with aging but in the treated soils, it was increasing with the resupply slower in *D.regia* treated soils than biochar treated soils.

This work has demonstrated that *D.regia* has the potential for simple, cheap and effective/efficient remediation of metal polluted waters and soils.

Contents

List of Tables

List of Figures

Chapter 1. Introduction

The role played by water to human and biological systems cannot be over emphasised. The majority of common fresh water sources available to local inhabitants in Nigeria are polluted, thus making access to clean water a serious problem (Galadima et al., 2011). Petroleum industries pose the greatest threat to water quality, several incidents of oil spills have occurred at different times and in various parts of the nation (Helmer et al., 1997). Lead poisoning by Galadima et al. (2011) and poisoning by nickel, manganese and chromium reported by Ibeto and Okoye (2010) have been associated with mineral exploration, these heavy metals have been ingested by consumption in drinking water and food (Adeleye and Adebiyi, 2003, Chukwu, 2008). Elevated concentration of heavy metals in ground water were reported (Adeleye and Adebiyi, 2003, Chukwu, 2008).

A study by Ogunkunle and Fatoba (2013) on the pollution loads and ecological risk assessment of soil heavy metals around a mega cement factory in Nigeria revealed that the concentration of lead, copper, cadmium and chromium were above the international standard limits. Slag disposal at the dumpsites of the three major automobile battery manufacturing companies in Nigeria have been reported to contribute greatly to soil pollution (Adie and Osibanjo, 2009).

There are several conventional methods of treatments of wastewater and contaminated lands. Adsorption has proved to be the best (Crini, 2005, Demirbas, 2008). All the methods are expensive and practically unaffordable by the small-scale industries in Nigeria. Recent studies have investigated the use of materials from natural sources as alternatives for the treatment of wastewater instead of activated carbon, though results obtained from the various studies were good, but the natural materials used had been

modified either by heat or chemical treatment. The modification of these natural materials, are regarded as additional cost of production and processing. In a country like Nigeria where the power supply is erratic and most supply of chemicals are basically by importation from developed nations, these additional costs cannot be underestimated. Thus, the investigation of an indigenous natural material in the unmodified state may be a great benefit to the country.

In this study, we aim to carry out investigation on the adsorption characteristics of *Delonix regia*, a natural waste material, a material without economic values, for reducing the available concentration of heavy metalsl from contaminated environmental systems. The heavy metals include Pb, Cu, Ni, Cd and Co. The *Delonix regia* materials were used for removing heavy metals from wastewater and treating contaminated soils by immobilising metals and reducing their bio availability. The efficiency of the remediation was assessed using conventional methods and a state-of-the-art dynamic technique, Diffusive Gradient in Thin Film (DGT).

To achieve the aim of this work the following objectives were set:

(a) investigate the effects of operating conditions such as pH, contact time, initial metal concentrations, ionic strength on the adsorption of metals in aqueous solution; determine the adsorptive capacities of *Delonix regia* for metals; investigate recovery capabilities of the bound metals from the used biomass;

(b) establish the kinetic and isothermal parameters of the adsorption process;

(c) investigate the potential of using *Delonix regia* material for soil remediation and establish a holistic programme of using DGT as a method to measure the available metals pre- and post- remediation;

(d) determine labile pool size and kinetic parameters of heavy metals in soils in selected sites in Nigeria using DGT and DIFS model.

Structure of the Thesis

Following this introduction chapter, the second chapter is a literature review. It highlighted various types, causes, effects and treatments of environmental pollution and focussed on the heavy metals and their deleterious effects to humanity and the ecosystem at large. It listed the demerits and merits of various treatment methods and dwelt extensively on the use of adsorption in remediation. It discussed past work and study undertaken in the use of materials from natural sources as alternative treatment methods and also as a source of activated carbon. The use of biochar in soil remediation was considered and a description of the Flame of the forest (*Delonix regia*) was given. Methods used for measuring and assessing availability of heavy metals in soils, including the new technique of DGT were elaborated.

Chapter 3 described the materials and the experimental procedures involved in the single-element investigation of the adsorption capabilities of *Delonix regia* pods. It also highlights on the various parameters obtained during the experiments while Chapter 4 provides the results obtained in the adsorption process using *Delonix regia* leaves, it discussed the effect of pH, contact time, initial metal concentrations and adsorbent dosage on the sorption process.

In Chapter 5, multi metals solution was used to spike soils and then treated with 2% w/w of biochar and *Delonix regia* pods at different aging time. Various methods for soil characterization were discussed. The efficiency of the remediation treatment with the use of hardwood biochar and *Delonix regia* was investigated with $CaCl_2$ (0.01M) and the results were compared between soils and between treatments.

Chapter 6 focuses on two major parts: the DGT measurements and using DIFS model to estimate the resupply kinetics of heavy metals in soils. It addressed the effect of different remediation treatment (*Delonix regia* and biochar) as it affects the availability of heavy metals (Pb, Cd and Cu) in soils, it also considered the effect of aging on the process. In this chapter, the combination of DGT measurements and DFIS modelling provided qualitative information for resupply of metals in soils and kinetics parameters such as response time and the dissociation rate constant of the process.

Chapter 7 provided the main conclusions from the thesis and some recommendations for further study.

Chapter 2. Literature Review

2.1 Environmental Pollution

Pollution of the natural environment is regarded as the release of contaminants into the environment in such a way that it results in harm or/and disorder in the global ecosystem (Gari, 2002), it could be classified mainly into three groups: Air pollution which is identified as the introduction of particles and chemicals into the atmosphere; Water pollution described to embrace surface runoff, liquid spills, waste water discharge and leakage into groundwater while Land pollution is the release of toxins on the land (Paoletti et al., 2010).

A pollutant is any material that contaminate air, water or soil; and the severity of its effects are determined by three factors namely: (i) Its chemical nature; (ii) Its available concentration (the concentration available to living organisms); and (iii) Its persistence in the environment.

Pollutants could be classed as biodegradable or non-biodegradable. Pollutants that are biodegradable in nature will not remain over long time in the environment, they can be used and decomposed by microbes, insects or other animals and birds, they can be converted into harmless products through biological activities. Examples of such pollutants are excreta, organic wastes, paper, and leftover food while those that are non-biodegradable will persist in the environment and cannot be converted to harmless products through natural activities examples are plastics and heavy metals.

2.1.1 *Water pollution*

Water is a very essential part of life. Fresh water is just a little percentage (3%) of the total water on earth, out of which 0.01% is available for human consumption (Hinrichsen and Tacio, 2002). The unsustainable use of water in agriculture and

industry, increase in population and urbanization have greatly affected the limited freshwater resources. The intentional or accidental discharge of wastewater arising from commercial and industrial activities into surface waters or when untreated sewage and chemical contaminants gain access into water bodies has caused water pollution. It could also be seen in the light of being the introduction of wastes into surface runoff thereby flowing into surface waters and consequently reaching to underground water sources (Aboyeji, 2013).

Sources of water pollution

Although during the hydrological cycle, natural water is capable of dissolving some heavy metals or trace elements (Ilyas and Sarwar, 2003), but the quantities into waters from anthropogenic sources (the several activities embarked by human) are the main cause of water pollution (Saif and Midrar-Ul-Haq, 2005). Indiscriminate disposal of municipal, industrial and domestic wastes in rivers, lakes, water channels and streams are the main activities leading to pollution (Azizullah et al., 2011).

All over the world, on a daily basis an estimate of over 2 million tonnes of wastewater and sewage are discharged into waters. A worse-case scenario is obtainable in developing countries, as 70% of untreated effluents and 90% of raw sewage are discharged into surface water (Azizullah et al., 2011). The major contributors to water pollution are industries such as ceramics, textiles, food industries, sugar industries, leather tanning, pharmaceuticals, steel, fertilizer factories, petrochemicals and oil mills (Sial et al., 2006). Large volumes of wastewater, in hundreds of thousands, containing cations and anions such as sodium, potassium, calcium chloride, carbonates and several other pollutants like nitrites, nitrates and toxic heavy metals like nickel, arsenic, iron, mercury, lead, cadmium, zinc, copper, chromium, cobalt and

magnesium are produced from their production operations (Sial et al., 2006, Ullah et al., 2009).

Waste originating from domestic and municipal sources and the extensive use of agrochemicals in agricultural activities are major sources of water pollution. Contamination of water by agricultural chemicals has been reported in countries like China (Li et al., 2014b). There have also been reports that increasing negative effects of water pollution have put more people at risk of carcinogenic diseases, potentially contributing to cancer villages, hot spots where cancer cases are exceptionally high (Lu, Song et al. 2015).

Many substances that are regarded as active water pollutants are classified into different groups. If they exceed a threshold value, they are deleterious and cause severe health problems in humans and other organisms. The most common among the groups are the pathogens (bacteria, viruses and protozoans), inorganic pollutants (acid, salts and toxic metals), anions (nitrates, phosphates, sulphates) and water soluble radioactive substances. Due to the toxicity, bioaccumulation, and low degradability, some trace metals like cadmium, lead, mercury, copper, chromium, zinc, nickel and arsenic according to Wang et al. (2017) have been listed as priory control pollutants by the United States Environmental Protection Agency. Although some heavy metals like copper, manganese, chromium are essential for human, their presence in excess may be toxic causing serious health effects (Govind and Madhuri, 2014).

2.1.2 *Soil Pollution*

Soil pollution is defined as the introduction of substances referred to as toxic chemicals (contaminants or pollutants) in soil in such concentration that the chemicals are capable of causing risk to human and/ or ecosystem health.

In addition, soil pollution occurs when levels of contaminants in soil are more than the limits that should be present, even though the level of contaminants in soil are not of risk (Wuana and Okieimen, 2011). As part of land degradation, soil pollution could be associated to the presence of xenobiotic chemicals in the soil environment. Industrial activities, agricultural chemicals, or improper disposal of waste typically causes pollution to soil, with the most common chemicals involved in soil pollution being solvents, heavy metals, petroleum hydrocarbons, pesticides and polynuclear aromatic hydrocarbons (e.g. benzo(a)pyrene and naphthalene). In several cases, soil pollution is correlated with the degree of industrialization and intensity of chemical usage.

The concern over soil pollution arises mainly because of associated health problems, especially when there is contact directly with contaminated soils, released vapours from pollutants, and because of polluted water supplies (Jinxia et al., 2010). Studies on trace metal accumulation, toxicity and persistence in agricultural soils have been widely conducted in soil and environmental sciences (Aelion et al., 2008). Arsenic, cadmium, lead and mercury can be harmful even at low levels when ingested over an extended period, triggering numerous illnesses including cardiovascular diseases and cancer (Bahemuka and Mubofu, 1999).

2.1.2.1 Effect of soil pollution

Increasing environmental concerns about the impact of trace metals on soil quality arose from the fact that they are responsible for more serious and long-time toxicity effects on soils with respect to other pollutant (Jinxia et al., 2010).

Trace metals are abundant in soils as they reside in soils for long periods and sequentially have potential damage to microbiota, flora, and fauna once they have

been transported from solid into solution or through biomethylation to organometallic moieties (Chen et al., 2015, Nriagu, 1996, Wei and Yang, 2010, Yang et al., 2009).

Farmlands are adversely affected by sludge application, untreated wastewater used for irrigation, atmospheric deposition and in some cases during waste transportation (Örnek et al., 2007, Saka et al., 2012). Mining activities destroy the natural landscape and also exposes the soil which has become barren of vegetation to erosion due to open cast mining (Dudka and Adriano, 1997). Multi-element contamination of the environment occurs from acid mine drainage (Dudka and Adriano, 1997). The presence of heavy metals in soil, reduces the pH of soil and surrounding water bodies by at least unit of 1 or 2 depending on the prevailing soil and environmental conditions (Dixit et al., 1992a, Dixit et al., 1992b). Top soil contamination by trace metal occur from the deposition of gases and dust from smelting operations (Merrington and Alloway, 1994). Heavy metal also reduces the abundance and biodiversity of soil microorganisms by its induced acidic soil condition thus lowering soil fertility and crop yield by altering carbon and nitrogen biogeochemical cycles (Dudka and Adriano, 1997). It renders contaminated land unsuitable for plant growth. Direct uptake of heavy metals from soil by plants or the direct deposition on plant leads to plant contamination, plant toxicity and there is potential transfer along the food chain (Dudka et al., 1996, Rebele et al., 1993). For example, the chronic low-level intake of soil metals through direct ingestion or indirectly through food, dermal contact or inhalation has negative effect on human health which may not be easily reversed through medical treatment (Li et al., 2014b, Ordóñez et al., 2011).

2.1.3 *Heavy Metal Pollution*

Pollution of heavy metals come from metal purification operations, for example, copper smelting; the preparation of nuclear fuels and manufacturing of printed circuit board. Petroleum refining, which is another source of heavy metal pollution, release metals such as, nickel, vanadium, lead, copper, zinc, aluminium, cadmium and chromium into the environment (Sörme and Lagerkvist, 2002) where they can be accumulated . One of the largest problems associated with the persistence of heavy metals is the potential for bioaccumulation and biomagnification, causing greater exposure for some organisms than the actual concentrations that is present in the environment alone (Watts, 2009).

Heavy metals are not biodegradable and they gain access into our bodies through, air, food, drinking water, or absorption in the skin by actual contact in manufacturing, agriculture, pharmaceuticals and industrial or residential settings (Cao et al., 2015, Kong et al., 2011), where they accumulate in both soft and hard tissues and become toxic because the body cannot metabolize them (Ghodbane and Hamdaoui, 2008). To produce toxic effects in the human body, high levels of exposure are not really necessary, since the accumulation of heavy metals occur gradually, and harmful effects increase when they exceed their threshold limits (Khuzestani and Souri, 2013, Pope et al., 2004).

Many metals such as cobalt, iron, zinc, copper, vanadium molybdenum and manganese are essential, but at elevated concentrations even the essential ones, are toxic because they cause oxidative stress by the formation of free radicals (Ghosh and Singh, 2005). Zinc is an essential element for human health, it regulates many biochemical processes and it is important for the physiological functions of living

tissues; but in excess, it results in skin irritations, anaemia, vomiting, nausea and stomach cramps (Oyaro et al., 2007). Copper plays an important role in animal metabolism; however, its excessive ingestion could cause serious health problems such as cramps, convulsion and even death (Paulino et al., 2006).

Metals are toxic because they can replace essential metals in pigments and enzymes thus disrupting organism functions (Henry, 2000). The presence of non-essential heavy metals in an organism cause significant alteration to its biochemical cycles. Metal ions bioaccumulated in the environment are biomagnified along the food chain and thus the toxicity is often more pronounced in animals at the higher trophic levels (Ahluwalia and Goyal, 2007) and due to its high solubility in the aquatic environments, living organisms can absorb them and they can become accumulated in high concentrations in the human body. There are various reports to the fact that heavy metals cause several disorders (such as cancer, chronic anaemia, cardiovascular diseases, damage to kidney, brain, bones and skin and cardiovascular diseases) in human being (Järup, 2003). The permissible limits of some metals in drinking water and sewage sludge are shown in Tables 2.1 and 2.2. Although using sewage sludge on agricultural lands is a general and acceptable practise in the UK, this practise is not applicable in Nigeria because there are limited facilities such as the sewer systems for treating domestic wastewaters. According to The Water Supply (Water Quality) Regulations 2016 at legislation.gov.uk and National Agency for Food and Drugs Administration Control, NAFDAC, Nigeria, these limits for each country are set based on the recommendations from WHO.

Table 2-1: Permissible limits of some metals in portable water (Duruibe et al., 2007, Kumar and Puri, 2012)

Heavy Metals	UK Max conc. (µg/l)	Nigeria Max conc. (µg/l)
Cadmium	5.0	3.0
Chromium	20	
Copper	2.0	
Lead	10	10
Mercury	1.0	1.0
Nickel	20	10
Arsenic	10	

Table 2-2: Permissible limits of some metals in sewage sludge (Nicholson et al., 2003)

Heavy Metals	Max limits in Sludges (mg/kg dry soil) in UK
Zinc	200
Copper	100
Nickel	60
Lead	300
Cadmium	3
Mercury	1
Chromuim	400
Arsenic	50

2.2 Water Remediation Treatment

Preventive measures to completely avoid exposure to these heavy metals are worthwhile and important, but ultimately futile. The inescapable reality is that it is impossible today not to be exposed to heavy metals, it is only a matter of how much and how often. Considering the health and environmental hazards caused by heavy metals, it is thus important to find means of cleaning them up from the environment. Currently, heavy metals are removed through various treatment methods which include; *In situ* –Phytoremediation, Electrodialysis, Ion exchange, Chemical precipitation, Ex situ-pump and treat, Reverse osmosis and Adsorption.

2.2.1 *Ex Situ: Pump and Treat*

Contaminated ground water has been remediated for a long time using the Pump and Treat method. The method involves using a pump for the removal of contaminated ground water and subsequently transporting it to a treatment plant where they are treated using conventional water treatment methods, after which the treated water can be re-injected into groundwater reservoir or discharged into rivers. The disadvantages of this method are the cost of pumping and treating the polluted water especially where the water is not effectively contained; intrusion into the groundwater reservoir, a major disadvantageous feature, is the long term consequence that occur as a result of removing the groundwater; an ever increasing volume of polluted water occur by dilution as a result of the inflow of treated or new groundwater (Das and Nassehi, 2001).

2.2.2 *Chemical Precipitation*

This is a very popular technology in the removal of heavy metals from water, it is the main method employed in industrial wastewater treatment. The method involves the

formation of insoluble solids from dissolved contaminants, thus enhancing their removal from water by physical methods of separation such as clarification and filtration (Saifuddin and Kumaran, 2005). In this method, particle sizes are increased through agglomeration when chemical precipitants like NaOH, $CaCO_3$ and lime (during neutralization) are added to the wastewater. Result from this process cannot be relied upon because complete hydroxide precipitation does not occur in the presence of complexing agents (Lee et al., 2006, Lee et al., 2007).

2.2.3 *Phytoremediation*

A process that involves the use of plants to partially or substantially remove selected substance in contaminated surface water, ground water and wastewater is referred to as Phytoremediation (Vangronsveld et al., 2009). Phytoextraction is an aspect of phytoremediation that occur when plants absorb, translocate and store contaminants as well as other nutrients and water. It is majorly used for treating wastes laden with metals (Lasat, 2000).

2.2.4 *Reverse Osmosis*

Reverse osmosis is a process in which a membrane, capable of removing more than 99% of all dissolved minerals, acts as a molecular filter. Water is allowed to pass through the membrane while particulate and dissolved matters are retained by the membrane, this is a very effective method when treating solutions containing ionic species. Wastewater held in a pressurized water storage is passed through activated carbon filter to remove organic compounds and then under pressure through a membrane which remove the contaminants (Akpor and Muchie, 2010). One of the major advantages of reverse osmosis over traditional treatment methods is that it can reduce both the concentration of other ionic contaminants as well as dissolved organic

compounds but the major challenge is that the membranes are relatively expensive to procure and the use of high pressure apart from increasing operation cost makes the technique highly sensitive to operating conditions (Bilal et al., 2013).

2.2.5 *Ion Exchange*

It is a reversible process where ions from wastewater or water are substituted for a similarly charged ions on an immobile solid particle called the ion exchanger. The ion exchanger particles could be the naturally occurring zeolites or synthetically produced organic resins mainly polymeric resins derived from hydrocarbon (Mier et al., 2001).

2.2.6 *Electrodialysis*

Electrodialysis is an electro membrane technique which involves the transport of ions from one solution to another through an ion permeable membrane under the influence of a potential gradient. The applied voltage across the two ends electrodes create the potential field necessary for electrodialysis to operate, charged ions are driven through the membranes made from ion exchange polymers. The membranes are selective and thus able to transport ions with positive or negative charge and reject oppositely charged ions. As a result, dialysis can be used for purposeful concentration and separation or removal of ions (Akpor and Muchie, 2010).

2.3 Adsorption

Adsorption has become the preferred choice over other methods of heavy metal remediation in wastewater because of the simplicity in its design, ease of scaling up and usage, it does not produce toxic pollutants and most importantly is its ability to remove pollutants at low concentration even at parts per million levels with high

efficiency (Awual et al., 2013, Carolin et al., 2017, Tang et al., 2013). The associated advantages of other physico-chemical processes are outweighed by a number of drawbacks listed in Table 2.3.

Adsorption is a mass transfer process which involves the accumulation of substance at the interface of two phases, such as liquid-liquid, gas-liquid, gas-solid or liquid-solid interface. The adsorbate is the substance being transfer from one phase to another while the adsorbent is the material on which accumulation occurs. The main processes involved in adsorption is depicted in Figure 2.1. The properties of both the adsorbate and the adsorbent are specific and depend upon their individual constituents (De Gisi et al., 2016).

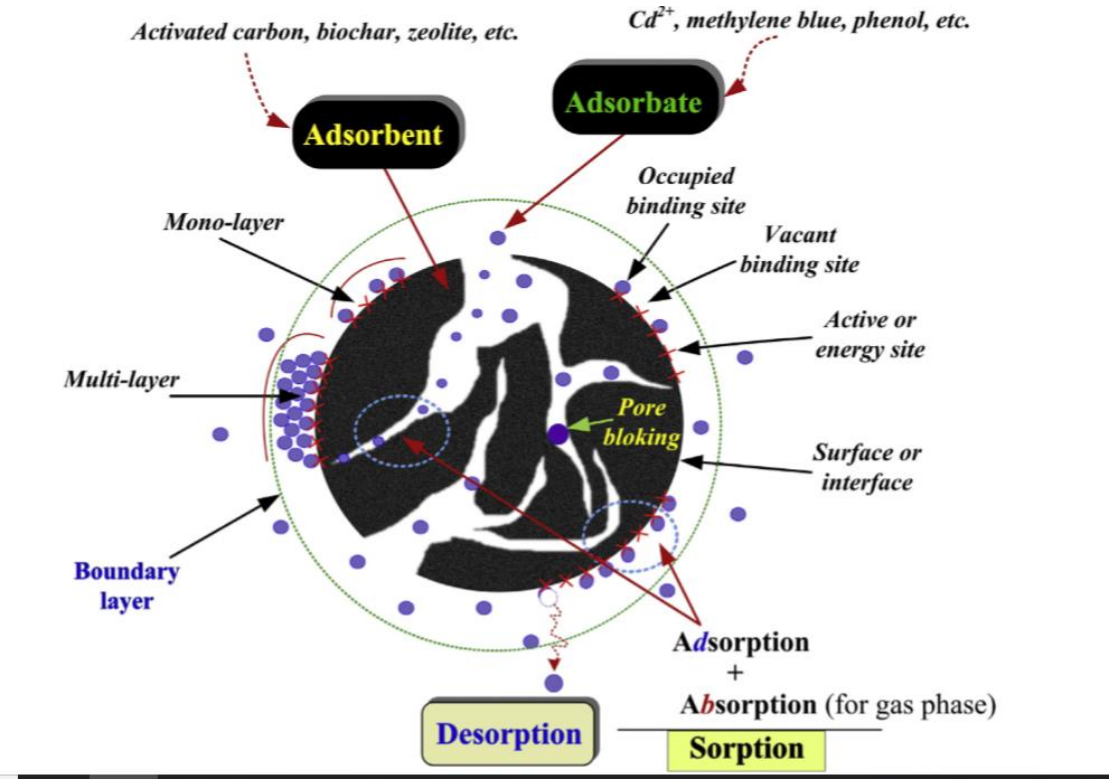


Figure 2-1: Processes and Terms involved in Adsorption Technology

Adsorption could be categorised into two types: (i) physical, where the adsorbate concentration increase at the interface is due to van der Waals forces of attraction in which case the resulting process is reversible and (ii) chemical adsorption is as a result of chemical reactions between the adsorbate and the adsorbent which leads to the formation of covalent or ionic bonds (Tripathi and Ranjan, 2015, Tyagi et al., 2017) Certain parameters such as pH, agitation speed, adsorbent dose, concentration of adsorbate, process temperature and ionic strength of the solution are factors that affect the sorption of metals.

In a solid-liquid system, adsorption results in the removal of solutes from solution and their accumulation at the solid interface. The solute remaining in the solution reaches a dynamic equilibrium with that adsorbed on the solid phase and the amount of adsorbate that can be removed by the adsorbent as a function of both temperature and concentration of adsorbate can be described by an adsorption isotherm according to the general equation 2.1.

$$Q_t = (C_o - C_t).{}^{V}/_{m} \quad \text{.....Equation 2-1}$$

Q_t (mg/g) is the amount of adsorbate per mass unit of adsorbent at time t; C_o and C_t (mg/l) is the initial concentration and at time t respectively; v is the volume of solution (l), and m is the mass of the adsorbent (g).

The commonly used isotherm models (Langmuir or Freundlich) for the adsorption of heavy metals are described in Section 3.3. During adsorption, adsorbate gets adsorbed onto the adsorbent and research findings indicate that metal ions can adsorb on activated carbon binding sites through a number of mechanisms such as direct bonding (Peng et al., 2017b), ion exchange (Dias et al., 2007, Sekar et al., 2004),

surface-complex formation (Kalavathy et al., 2005), Cπ-cation interaction (Khan and Wahab, 2007) and coordination to functional groups (Kobya et al., 2005).

The electrostatic attraction between the positively charged heavy metal ions and the negatively charged ion on the adsorbent provides the driving force for the adsorption process. It's been reported that electrostatic attraction is the main contribution to the adsorption of Zn on graphene oxide (Wang et al., 2013a). Ion exchange reactions between heavy metal ions and the proton on -COOH or -OH functional groups on adsorbent is a mechanism for adsorption that is reported for Pb (Cao and Li, 2014). Surface complexation between heavy metal ions and the surface of oxygen containing functional groups had been confirmed to play a dominant role in adsorption (Peng et al., 2016). Three main steps are generally involved in sorption of pollutants onto solid adsorbent:

(i) pollutant transport from the bulk solution onto the sorbent surface;

(ii) adsorption on the sorbent surface; and

(iii) transport of pollutants within the sorbent particle.

Various types of adsorbents have been modified for use in the remediation of heavy metals from wastewater but the main aspects necessary for the selection of adsorbents are cost effectiveness and which adsorbent is most appropriate for the technology (Vunain et al., 2016). The main properties of adsorbent to be considered for the efficiency of the adsorption process are pore size distribution of the adsorbent particles, high surface area, functional groups, and the polarity of the adsorbent (Ruihua et al., 2011). Adsorption is often accompanied with the reverse process – desorption, which represents the transfer of adsorbate ions from the adsorbent surface to the solution. Desorption of used adsorbents can be achieved by thermal

regeneration, pressure swing method and electrochemical regeneration and the regenerated adsorbent can be reused for several purposes (Carolin et al., 2017).Various types of adsorbents have been modified for use in the remediation of heavy metals from wastewater but the main aspects necessary for the selection of adsorbents are cost effectiveness and which adsorbent is most appropriate for the technology (Vunain et al., 2016). The main properties of adsorbent to be considered for the efficiency of the adsorption process are pore size distribution of the adsorbent particles, high surface area, functional groups, and the polarity of the adsorbent (Ruihua et al., 2011).

In the adsorption process, adsorbents can be recreated by the desorption process because it is a reversible technique and the regenerated adsorbent can be reused for several purposes. Regeneration of used adsorbents can be achieved by thermal regeneration, pressure swing method and electrochemical regeneration, based on the regeneration, adsorption is considered as an environmentally acceptable method (Carolin et al., 2017).

Table 2-3: Physico-chemical processes involved in the treatment of waste water adapted from Carolin et al., 2017

S/No	Techniques	Advantages	Disadvantages	References
1	Coagulation	Cost effective	Generation of sludge, Utilization of chemicals is high	(Ahmed and Ahmaruzzaman, 2016)
2	Membrane filtration	High removal of heavy metals, lower space requirement	Very expensive, membrane fouling, complex process	(Ahmed and Ahmaruzzaman, 2016)
3	Adsorption	Easy operation, less sludge production, utilization of low cost adsorbents, Desorption	Process control is governed by the diameter of the pores and the diffusion rate of the molecules through the pores.	(Ruihua et al., 2011)
4	Electrochemical treatment	Efficient for the removal of important metal ions, low chemical usage	High initial investment, high electrical supply	(Ahmed and Ahmaruzzaman, 2016)
5	Electrodialysis	High segregation of metals	Clogging and energy loss	(Ruihua et al., 2011)

6	Photocatalysis	Eliminates both the metal ions and organic pollutants concurrently	It takes long time to remove the metals	(Nguyen et al., 2013)
7	Ion exchange	High transformation of components	Removal of limited metal ions, high operational cost	(Farooq et al., 2010)
8	Oxidation	No need of electricity	Rusting occurs in the system due to oxidation	(Patil et al., 2016)

2.3.1 *Adsorption on activated carbon*

Activated carbon is the most effective sorbent for removing heavy metals from a wide range of industrial and municipal wastewater, contaminated groundwater and landfill leachate. (Ahmaruzzaman, 2008). The raw material and the particular activation process used affect the properties of the activated carbon. Heavy metal adsorption onto activated carbon is greatly influenced by the chemical and physical properties of the activated carbon. Such characteristics include pore space volume, ash content, specific surface area and surface functionalities (Carolin et al., 2017). In order to increase its capability of adsorbing the heavy metals different researches have been done to alter the properties of the activated carbon. Such researches include packing of AC with nanoparticles (Asfaram et al., 2015), installation of functional groups like nitrogen groups (Kang et al., 2016, Moreno-Tovar et al., 2014).

Commercial activated carbon pellet was chemically modified to remove cadmium from solution and it was reported that maximum cadmium uptake of 88% was obtained at pH 4.5 to 6.5 and the adsorption capacity is 25.1mg/g during a four-hour contact time (Bian et al., 2015).

In 1984, Netzer and Hughes explained in their work on ten different types of activated carbon for the removal of lead, copper and cobalt from solution that solution pH played an important role in the sorption of each of the studied metals to any of the activated carbon used in their study. An optimum pH of 4 was used for the sorption; a contact time of 30 minutes was sufficient for the removal of copper and lead, but cobalt removal was found not to be effective until 120 minutes of contact. There was significant difference in the ability of the activated carbons to adsorb lead, copper and cobalt with average percentage removal being 92%, 80% and 81% respectively (Netzer and Hughes, 1984).

2.3.2 *Adsorption on new adsorbents*

There have been great interest and focus in the research for removing heavy metals from industrial effluents by using low-cost adsorbents like agricultural by-products such as sawdust, coconut shell, chitosan, mango leaves, egg shells as adsorbents (Örnek et al., 2007, Saka et al., 2012).

Bio-sorption sometimes defined as the use of agricultural by-products in remediation, utilizes active and inactive (non-living) biomass to sorb and concentrate heavy metals from waste streams by purely physico-chemical pathways (mainly chelation and adsorption) of uptake (Mustapha et al., 2014). In biosorption process, both living and non-living biological materials are used to remove the heavy metals. (Carolin et al., 2017). Biosorbents are considered to be a low-cost adsorbent, feasible (that is easy to

modify) and can be obtained from various sources (Gadd, 2009). After chemical modification or conversion to activated carbon by heating new materials like rice husk, hazelnut shell, jackfruit, pecan shells maize cob or husk, could be used as adsorbent for heavy metal and organics removal from wastewater. Some other waste materials used as adsorbents are coconut shell, bark and other tannin-rich materials, fruit wastes, scrap tyres, woody materials, fertilizer wastes, sugar industry waste, petroleum wastes, fly ash, blast furnace slag, seafood processing wastes, clays, peat moss, zeolites, red mud (Ali et al., 2013, Fu and Wang, 2011). The presence of some specific functional groups like aldehydes, ketones, ether, phenol and carboxyl on the biosorbents enhance its adsorption activity for pollutant removed (Demirbas, 2008). The crucial factors affecting the potential of any biosorbent are pH, temperature, adsorbent dosage, metal ion concentration, contact time, ionic strength (Demirbas, 2008).

2.3.2.1 Adsorption by Algal Biomass

Researchers have recently focussed on living and non-living algal biomass for treatment of heavy metal wastewater (Areco et al., 2014, Lee and Chang, 2011, Liu et al., 2009) because algal biomass contains active functional groups that improve biosorption capabilities on their cell wall surfaces.

Living biomass have limited adsorption capacity because the adsorption process is occurring in the growth phase and this being an intracellular process makes adsorption mechanism more complicated. For non-living algae biomass, the uptake of heavy metal is known to be an extracellular process because the metals are adsorbed on the surfaces of the cell wall (Areco et al., 2012). Environmental factors like pH and

temperature can affect the adsorption capacity of non-living algae (Zeraatkar et al., 2016).

The powdered form and activated carbon prepared from a marine alga, *Ulva lactuca* was used by Ibrahim et al. (2016) to remove Cu^{2+}, Cd^{2+}, Cr^{3+} and Pb^{2+}. The removal efficiency obtained were 64.5 and 84.7mg/g for copper, 62.5 and 84.6 mg/g for cadmium, 60.9 and 82mg/g for chromium and 68.9 and 83.3mg/g for lead by using the powdered and activated carbon from *Ulva lactuca*.

2.3.2.2 Adsorption by Low Cost Adsorbents

The aforementioned adsorbents are inexpensive and renewable; however, they have a disposal problem, and this poses a limit to their usage. The search for cheaper adsorbents continued and researchers mainly focussed on the use of low cost adsorbents from industrial by-products, agricultural wastes, and other natural substances for heavy metal removal (Chu et al., 2015). The utilization of low cost adsorbents in the adsorption process is studied and regarded as a new technique in wastewater treatment.

Agro-wastes generally comprising of agricultural waste and plant materials act as substitute for the conventional adsorbents and their use in wastewater treatment is an efficient, eco-friendly, cheap and easy method in the reduction of heavy metals loads in wastewater. Various agricultural waste biomass like the shells of cashew nut, palm oil fruits, orange peels, barley straw and garden grass have been used in order to recover heavy metal from wastewater (Feng et al., 2010, Hossain et al., 2012a, Pehlivan et al., 2008, SenthilKumar et al., 2011).

Major components of agricultural wastes are cellulose, lignin, and hemicellulose which contains the hydroxyl functional group and improves the affinity of the biosorbent towards the metal ions. They also comprised of other functional groups like amido, amino, carboxyl, acetamido, phenolic and esters, which play a crucial role in the replacement of hydrogen ions of the metal and formation of complexes (Yan et al., 2010).

Anastopoulos et al. (2017) reviewed the use of waste obtained from sugar bagasse for the removal of heavy metals and reported that the optimum adsorption condition for the removal of $Mn^{2}+$ were pH 6, adsorbent dose 1.5g, and equilibrium contact time of 150mins. He studied the work of Moubarik and Grimi (2015) for the uptake of cadmium by sugar bagasse noting that the best sorption was achieved at pH 6, an equilibrium time of 25 minutes and that percentage adsorbed was increased from 87 to 96% when the adsorbate concentration was increased from 10 to 30mg/l.

Pérez-Marín et al. (2007) also gave a report from his study on the use of bagasse for cadmium removal that maximum adsorption was achieved at 150rpm of agitation, pH between 5 and 7 and contact time of 90 minutes. Aksu and İşoğlu (2005) reported a removal efficiency of 10.8 to 24.6mg/g for copper sorption to bagasse in the pH range of 2 to 4, he reported a decrease in sorption when the pH is greater than 4.

At pH 4 and for 12 hours contact time, chemically modified dried banana peel have adsorption capacity of 19.70mg Cu/g; indicating 89.01% as efficiency of removal (Hasanah et al., 2012). Castro et al. (2011) studied the removal of copper and lead from solution using grounded banana peel, he found that equilibrium was achieved within 10mins and that pH above 3 is favourable for the process; the maximum adsorption capacities of 20.97mg/g and 41.44mg/g were obtained for copper (II) and

lead (II) respectively. Ogunleye et al. (2014) reported that capacity of 13.53mg/g was obtained when acid treated banana stalk was used for the removal of lead from aqueous solutions.

Sudha et al. (2015) stated that the AC got from Seed Carbon (prepared from waste such as seeds and peels of citrus limettioides) had the capacity of 35.54g/g for removal of nickel at pH 6.5 and 240 minutes of contact. Peanut hulls used for the removal of nickel from aqueous solution and nickel plating industrial wastewater showed 53.6mg/g adsorption capacity at pH 6.5 and adsorbent dose 100g/100ml at 90 minutes contact time. Coir pith from coconut industry was used by (Ewecharoen et al., 2008) to remove nickel from electroplating rinse water. Optimum conditions of pH 4-7, equilibrium contact time of 10mins, temp. 30^{o}C and capacity of 9.5mg/g were reported for the unmodified coir while 38.9mg/g was reported for the modified coir under similar conditions.

2.4 Soil Remediation

Metal polluted soils can be treated or remediated by biological, chemical or physical methods, which can be grouped into two categories Ex-situ methods and In-situ methods (Shaw, 1989).

The ex-situ methods require that the contaminated soil is removed and treated either on or off site and returned after treatment to the resorted site. It encompasses excavation, destruction and or detoxification of contaminants chemically or physically and its subsequent stabilization, solidification, immobilization, incineration or destruction.

In-situ is basically on-site remediation, it is defined as the technologies that involve destruction or transformation of contaminants, immobilization to reduce bioavailability and separation of the contaminant from the bulk soil (Vandegrift et al., 1992). Generally, it is preferred over the ex-situ approach due to lower cost involvement and reduced impact on the ecosystem.

2.4.1 *Physical Treatment*

Physical remediation involves the process of reversal or actual stopping of damage to the environment by using physical technologies such as capping, flushing or thermal treatment.

Electrokinetics: In Electrokinetics an electric current gradient initiates the movement by electro-migration (movement of charged chemicals), electro-osmosis (fluid movement) electrophoresis and electrolysis (Rødsand et al., 1996).

Electrokinetics process incorporate passing a low intensity electric current between a cathode and anode imbedded in the contaminated soil, ions and small charged particles and water are transported between the electrodes. Negatively charged ions are moved towards the positive electrode and the positively charged ions are moved towards the negative electrode. The deposited metals can be removed from the electrode by electroplating or precipitation / co-precipitation (Smith, 1995).

The Electrokinetic remediation method is a good choice for soils with low permeability, it is economically effective because of ease of operation (Virkutyte et al., 2002) and does not destroy the nature of the soil (Page and Page, 2002). Its limitation for direct usage is fluctuation in soil pH because it can’t retain the soil pH value.

Thermal: The application of high temperature to highly contaminated soil (5-20%) can be used to reduce the mobility of heavy metals (Mallampati et al., 2015). High temperature such as 200^{o}C -700^{o}C are required for the formation of vitreous and volatile materials which are afterwards recovered or immobilized.

Thermal treatment or phyrometallurgical separation is especially useful where metal recovery is profitable. The soil is first concentrated by physical method or soil washing before being transported off site for phyrometallurgical processes. Gold and platinum can be recovered from low soil concentration using this process (Mulligan et al., 2001). The in situ thermal treatment requires heating the subsurface for improving the mobilization, volatilization and destruction of contaminants in soil. Methods of heating applied may include conductive heating, radio frequency heating, electrical resistivity heating and steam-based heating (Samaksaman et al., 2016, Triplett Kingston et al., 2012).

Soil Isolation is a means of separating the soil contaminated with heavy metals from uncontaminated soil, and afterward auxiliary engineering measures are carried out for complete remediation (Zheng and Wang, 2002). It is carried out basically to prevent off-site movement of heavy metals by containing and restricting them within a specified area (Zhu et al., 2012). It is done to avoid further contamination of groundwater by heavy metals when other remediation methods are not physically or economically feasible.

2.4.2 *Chemical Treatment*

Chemical remediation or treatment is a method in which chemical reagent, reaction and principles are applied and used to remove contaminants. The mechanisms

involved include adsorption, catalysis, ion exchange oxidation, reduction (Kang et al., 2016, Mao et al., 2015, Usman et al., 2012).

Efforts have been put into developing chemical remediation methods for in situ remediation of contaminated soil and sediment, with biochar and activated carbon showing to be effective by causing a reduction of both organic and inorganic pollutants in porewater (Choi et al., 2014, Gomez-Eyles et al., 2013).

Immobilization technique

Heavy metal immobilization in soil is done to reduce their leachability through pH and alkalinity control in order to minimize their solubility or basically by promoting adsorption, ion-exchange, complexation and precipitation of pollutants (Stegmann et al., 2013). It involved adding immobilizing agents to the contaminated soil. The processes involved in immobilization techniques can cause a redistribution of heavy metals from soil solution to soil particles and it is thus able to limit their transport and bioavailability in the soil (Khalid et al., 2017). Immobilization of heavy metal in soil is done by amending the contaminated soils with organic or inorganic amendments (such as cement, zeolites, microbes, clay, phosphates (Austruy et al., 2014, Shahid et al., 2014c). Adding organic amendment as a means of immobilizing heavy metals is effective at the initial stage of application but its immobilization effects on metal bioavailability varies over time due to decomposing of organic matter. The use of low cost industrial residues like Industrial egg shell (Soares et al., 2015), red mud (Smičiklas et al., 2014) and termitaria (Anoduadi et al., 2009) have been investigated for heavy metal immobilization in contaminated soils.

The effective immobilization of nickel, lead, manganese, chromium, and iron by Farm Yard Manure and copper, zinc and cadmium by di-ammonium phosphate was reported

by (Khan et al., 2015). Organic amendments have high affinity for metal complexation because the composition of organic amendment are mainly lignin and cellulose others are proteins, simple sugars, hemicellulose, lipids, hydrocarbon with various functional groups such as phenols, acetamido groups, carbonyl groups, amino, esters, structural polysaccharides and amido (Niazi et al., 2016). The formation of metal-organic matter complexes is dependent on the type and nature of the organic matter (Shahid et al., 2014a). It has been reported that heavy metal immobilization by organic amendment may be as a result of increase in soil pH by preventing sulphide oxidation or hydrolysis (Walker et al., 2004) and also by increasing surface charge (Gadd, 2000).

Soil Washing

This refers to processes that can result in the leaching of heavy metals from soil and consequently lead to their removal when various extractants and reagents are used on contaminated soils. Soil washing is a rapid method which can meet specific criteria without any long-term liability (Park and Son, 2017). Soil washing with suitable extractants for leaching heavy metals have proved to be a good alternative to some of the clean-up techniques used for contaminated soils. It involves digging out the contaminated soils and mixing it with a solution of suitable extractant (depending on soil and type of metal) for a specified time. The metals in soil are transferred from soil solid phase to liquid phase by, ion exchange, desorption or chelation and then can be separated from the leachate (Ferraro et al., 2015).

Soil washing reagents include synthetic chelating agents such as ethylenediamine tetra acetic acid (EDTA), humic substances, organic acids, surfactants (Kulikowska et al., 2015, Shahid et al., 2014b), high concentration of salt chloride solutions like iron (III)

chloride and calcium chloride (Makino et al., 2008). Rinsing steps, repeated washing and the combined use of different chelators improves heavy metal washing efficiency especially in multi-metal contaminated soil (Guo et al., 2016). Removal efficiency of 41.9% of arsenic and 89.6% of cadmium was achieved when phosphoric-oxalic acid Na_2 EDTA was used for soil washing (Wei et al., 2016).

2.4.3 *Biological Treatment*

Biological remediation is the cleaning up of environmental pollutants by the aid of biological processes and reactions. This include phytoremediation, bioaugmentation, bioventing, biosparging and biodegradation. Recent research into the effectiveness of phytoremediation and bioaugmentation of soil contaminated by heavy metals and petroleum showed that the heavy metal content in the plants used for the pot experiments were limited; the translocation of the heavy metals was poor showing that they were concentrated majorly in the root (Agnello et al., 2016, Cai et al., 2016).

Phytoremediation

Phytoremediation is considered as a green technology with good public perception and it is widely used for the removal of pollutants, heavy metals in particular. The technology uses green plants and their associated microbial communities to remove, degrade or stabilize inorganic or organic contaminants.

Phytoremediation is one of the cheaper options to re-establish natural soil conditions, it involves using the catabolic potential of plants root or associated microorganisms to reduce, remove or detoxify heavy metals from the soil (Greipsson, 2011). Compared with other methods of remediation, phytoremediation has low installation and maintenance cost (Van Aken, 2009), can cost as less as 5% of alternative clean-up methods (Prasad, 2003). Selection of fast growing plants and the longer times required

compared with other methods are major limitations of this treatment method (Mulligan et al., 2001). Phytoextraction, phytostabilization, phytovolatilization and phytodegradation are the strategies involved in phytoremediation.

Phytoextraction is the most useful phytoremediation technique for metal removal from polluted soils. It is the uptake of contaminants from soil by the roots of plants and their translocation to accumulation in the shoots (Sekara et al., 2005). Bioavailability and speciation of heavy metals in soil, soil properties and plant species are factors that affect the efficiency of phytoextraction.

2.5 Risk Assessment of heavy metals in soil

It is essential to conduct risk assessment of pollutants in soils before and after remediation and one of the important parameters is bioavailability of pollutants. Bioavailability refers to the biologically available chemical fraction (pool) that can be taken up by an organism and that can react with its metabolic activities (Campbell et al., 1995), or it may refer to the fraction of the total chemical that is able to interact with a biological target (Vangronsveld, 1998). For the pollutants (metals) to be bioavailable, there must be physical accessibility (that is it must have come in contact with) between it and the organism, and also the pollutant has to be in a particular form for it to be able to enter the root of a plant or the body of an organism. Simply said, a pollutant has to be mobile, be able to transport across a semi-permeable membrane and be in an accessible form for it to become bioavailable.

2.5.1 *Indicator for bioavailability*

Possible methods for the determination of the bioavailable and bioaccessible fractions can be put under three main groups:

- methods for assessing metal concentration in soil solution or pore water; including assessment of metal speciation and the activity of the free metal ion;
- single and sequential extraction methods;
- methods for determining total metal content in soil or sediments by rigorous digestion.

An estimate of the bioavailable and accessible fractions of metals can be provided by the methods for assessing metals in pore water; whereas extractions and digestions may provide an estimate of potentially available and accessible fractions (Templeton et al., 2000).

2.5.1.1 Assessment in pore water or soil solution

The major route by which plants, microorganisms and soft-bodied organisms become exposed to heavy metals is from the soil solution because nutrients and contaminants including dissolved heavy metals are readily available and taken up through the root tips and their soft bodies from soil solution. As a result, the determination of total dissolved elements in soil (fractions which can be expressed in terms of the concentration of the free metal ion and the concentration of other ions that are involved in the direct uptake) has been recognised as a method for measuring heavy metals toxicity and bioavailability in soils (Parker and Pedler, 1997, Pavan et al., 1982). Heavy metals in soil solution exist in forms such as complexes with a lot of inorganic ligands and naturally occurring organics, free hydrated ions and bound to colloidal particles, thus soil solution speciation is important in bioavailability (Hooda, 2010).

The concentrations/activities of free ions can be measured by ion-selective electrodes, ion-exchange resins, Donnan membrane systems and anodic stripping voltammetry. All these methods have been applied to measure heavy metals speciation in soil solution (Zhang and Young, 2005). Despite the advances in the use of these techniques to measure free ion activity of trace elements, ion-exchange resins, Donnan membrane systems and voltammetry have suffered from either chemical interference, poor limits of detection or disturbance of solution equilibrium (McLaughlin et al., 2000, Nolan et al., 2003). The use of ion-selective electrodes has been reported to be very successful but limited to Cu (Christl and Kretzschmar, 2001, Sauvé et al., 1995), not much sensitivity is recorded for Cd (Kaschl et al., 2002), Pb (Christl and Kretzschmar, 2001) and Zn (Morley and Gadd, 1995). Voltammetry techniques are not species specific, i.e. gives a measure of all the labile species in the soil solution, and are not easily calibrated (Florence, 1986, Sauvé et al., 2000). Speciation by free ion activity using ion-exchange resins is operationally defined, because organic and inorganic metal complexes can contribute to the measurement (Persaud and Cantwell, 1992). The Donnan dialysis system uses ion-exchange in the form of a membrane (Helmke et al., 1997, Temminghoff et al., 2000).

Many studies have reported that there have been strong correlations between the free metal ion concentration and uptake of metal ions. In 2002, (Slaveykova and Wilkinson) found a strong relationship between the free lead concentrations and lead uptake by algae, rather than the total lead concentrations. Based on such observation, the free ion activity model (FIAM) and its subsequent adaptation, the biotic ligand model (BLM) have been developed (Playle, 1998). The FIAM operates on the basis that the free ion activity is the determining factor in the uptake. Generally, it was accepted that plants uptake of nutrients and consequently trace metals is related to

their free ion activities in the solution, until in recent times, when there is considerable evidence which challenged the free ion activity concept (Jiang et al., 2003, Krishnamurti et al., 1997, Leyval and Berthelin, 1993, López et al., 2005, Marschner and Römheld, 1983, McLaughlin et al., 1994, Nolan et al., 2003, Weggler et al., 2004).

The dynamic processes (such as the soil capacity, or labile fractions present in solution to supply that element) necessary for maintaining the free metal activity were not considered and this is a limitation for predicting the bioavailability of metal when using the free metal activities in solution (Parker and Pedler, 1997).

2.5.1.2 Extraction

Extraction can be defined operationally as a technique that is used to assess the amount of metal in the solid phase pool that can be re-supplied to the solution of the metal concentration, thus behaving like the concentrations of labile metal that are available for uptake by plants or biota. Examples include the use of calcium chloride aqueous solution to mimic uptake of metal by earthworms or plants (Gupta and Aten, 1993); extractions stand as intermediate between soil solution samples and total digestion samples. Many researches on the behaviour of metals in sediments and soils have focussed on the use of different extraction chemicals to describe the species of metals present.

In broad terms, six types of extractions may be identified, they are:

- weak salt extractions e.g $CaCl_2$, $Ca(NO_3)_2$, NH_4Ac, $NaNO_3$. These are used in a range of concentrations from 0.001M to 1M;

- reductive extractions like sodium ascorbate, HCl, hydroxylamine, sodium dithionite;
- weak acid extractions e.g acetic acid, citric acid;
- strong complexation methods (e.g. ethylene diamine tetraacetic acid, EDTA, diethylene triamine pentaacetic acid, DTPA-TEA);
- dilute strong acid e.g HNO_3, double acid ($HCl + H_2SO_4$);
- combined extractants (e.g ammonium oxalate-oxalic, Melich III (dilute acid, salt, and EDTA) (Bakircioglu et al., 2011, Basta and Gradwohl, 2000).

There are clear differences among extraction techniques in respect to simulating bioaccessible and bioavailable portions. A particular technique may give a good result of the bioavailable portion for a type of plant but may not be able to give a good result for other plant types. In a wider range of soil characteristics or metal concentrations, extraction techniques usually fail to adequately predict metal bioavailability and also the chemical extraction methods are not specific in operation (Peng et al., 2017a).

2.5.1.3 Digestion

Most digestion to determine the totally recoverable metal content in soils involve the use of concentrated mineral acid and elevated temperatures. In order to prevent the destruction of the soil crystal structure during digestion, the temperatures and type of acid used should be considered. Apart from the fact that hydrofluoric acid is very dangerous to work with, when it is added to the digestate in total metal digestion, crystal lattices are broken down and the metals bound or trapped in these structures, which ordinarily will not be available to plants, are extracted as well. The

concentrations obtained by this approach cannot represent the bioavailable fraction and it is therefore not an appropriate measure for bioavailability of pollutants.

Other approaches to assessing the risks from trace elements in soils, including the effectiveness of remediation treatments such as formation of stable metal minerals are X-ray-Based Spectroscopic Techniques (Gräfe et al., 2014, Kim et al., 2003), Isotopic Dilution Techniques (Young et al., 2005) and Diffusive Gradients in Thin Films (Davlson and Zhang, 1994).

2.6 Diffusive Gradient in Thin-Film (DGT)

2.6.1 *DGT and Bioavailability*

The DGT technique, first reported in 1994 by Davison and Zhang is another method used for measuring effective pore water concentrations and metal supplied from the solid phase (Davlson and Zhang, 1994, Zhang et al., 2001). The use of passive sampling devices such as (DGT was suggested to be a chemical alternative or supplement to biomonitoring for measuring and assessing metal bioavailability in terrestrial and aquatic systems (Montero et al., 2012, Schintu et al., 2010). Using DGT in the assessment of chemical bioavailability has been developed on the basis that testing soil solution using the conventional methods have these shortcomings: (a) in the course of sampling and extraction, speciation of metal may change and (b) no consideration was made for metal re-supply kinetics.

The DGT method operates on the principle, that a depletion of soil solution concentration of metals (because of uptake by plants) stimulates the resupply of metal from species in the solid phase principally by diffusion (Nolan et al., 2005) and useful

information about resupply of metal from the solid phase to solution can be adequately provided by the DGT.

The metals accumulated by DGT are expected to be strongly similar or representative of that taken up by plants if diffusion is the main mechanism responsible for metal resupply from the soil. Another advantage of the DGT technique is that it is able to integrate the concentration of bioavailable metals in soil solution with kinetics of metal supply from the solid phase (Nolan et al., 2005). Thus, the mass of accumulated metal by the DGT is from both the solid phase and solution that are labile and responsive to depletion adjacent to the DGT device (Agbenin and Welp, 2012).

DGT has the advantage that it can be used for in situ determination and it can mimic the actual root environment (Tian et al., 2008) and thus it easily measures not only the concentration of labile metals in soil solution but also the dynamic diffusible supply of metals from the organic and inorganic complexes and from the soil solid phase (Davison and Zhang, 2012, Zhang et al., 2002). Some studies have shown the superior ability of DGT to detect heavy metal concentrations compared with traditional extraction methods, DGT measurement more accurately reflected metal uptake by plants (Yao et al., 2017, Zhang et al., 2002, Zhang et al., 2004a, Zhang et al., 2001).

Another advantage associated with the DGT is that DGT devices with different diffusive gel thickness can be used to generate different diffusion gradients or uptake fluxes and subsequently different rates of demand for metal ions (Peijnenburg and Jager, 2003). DGT demand is determined by the diffusive gel layer thickness and the initial concentration in soil solution. As the diffusive gel layer becomes thinner, the demand becomes greater and the fully sustained case may become partially sustained. The result is that DGT is able to maintain a steady-state concentration in the soil

solution as a result of the flux from soil to solution, providing the DGT demand is kept relatively low by having thicker gel membranes clearly demonstrates that kinetically labile solid-phase metal contributes to plant uptake, which, unlike soil solution, free metal activity or isotopic dilution, is included in the DGT measurement. The technique has proved a better predictor of plant available metal as it provides a measure of the labile metals in solution as well as their kinetically labile pool associated with the soil solid phase (Hooda and Zhang, 2008, Zhang et al., 2001). In the same vein, other competitive ions which affect plant uptake in other bioavailability methods have no bearing on the DGT-measured flux (Zhang et al., 2004b).

2.6.2 *DGT principle in solution*

In the DGT samplers, metal ions diffuse freely through a well-defined hydrogel layer and are subsequently immobilised in a gel impregnated with an exchange resin. DGT samplers are able to pre-concentrate dissolved metals providing a time-integrated measure of their concentration in the water during the deployment period. In the DGT, only labile dissolved metal species such as ionic forms and weakly dissociable complexes (also called the DGT-labile fraction) are measured, these metal species from the bulk solution diffuse across the filter membrane and the diffusive hydrogel until the metal is bound to the binding resin embedded in the poly-acrylamide gel (Zhang and Davison, 1995).

The DGT technique incorporates an ion exchange resin separated from the solution by an ion-permeable gel membrane (Figure 2.2). Mass transport through the gel is diffusion-controlled and thus well defined, making it possible to obtain quantitative data on speciation and concentration over relatively short period of time (from one hour to several weeks). Transport in the gel is restricted to diffusion and by selection

of an appropriate gel thickness, it controls the overall rate of mass transport irrespective of the hydrodynamics in the bulk solution (Davlson and Zhang, 1994). Chelex-100 resin gel has been used in DGT to provide measurements of metal concentrations. Chelex-100 is a cation exchange resin selective for trace metals and closely packed in a single layer on a 75-150μm sphere. The DGT method, cross-section shown in Figure 2.2, relies on measuring a flux of metal over a given time, it depends on establishing a defined concentration gradient in the diffusion layer, the thickness of which is represented as Δg. The concentration of metal ions at the interface of resin gel and diffusive gel is effectively zero due to the efficient uptake of the metal ions. The diffusive boundary layer (DBL) of thickness δ, at the surface of a DGT device is assumed negligible as δ<< Δg. Therefore, the Fick's law of diffusion can be used to define the flux of a given metal ion as shown in equations 2.2 and 2.3, where D is the diffusion coefficient of the metal ions and C_b is the concentration of the metal ions in bulk solution.

$$Flux = \frac{DC_b}{\Delta g} \quad \text{.....Equation 2-2}$$

The flux is defined as the mass (M) per unit area of diffusion (A) per time t.

$$Flux = \frac{M}{At} \quad \text{..... Equation 2-3}$$

Therefore, the concentration of metal ions in the solution can be quantified by equation 2.4:

$$C_b = \frac{M\Delta g}{DAt} \quad \text{.....Equation 2-4}$$

Provided the resin is not saturated, the longer such a device is immersed in solution, the more metal will be accumulated and making analysis easier. The more analyte concentration available for analysis, the easier it is to avoid the below instrument

detection limit and more reliable and better the result will be located in the calibration curve.

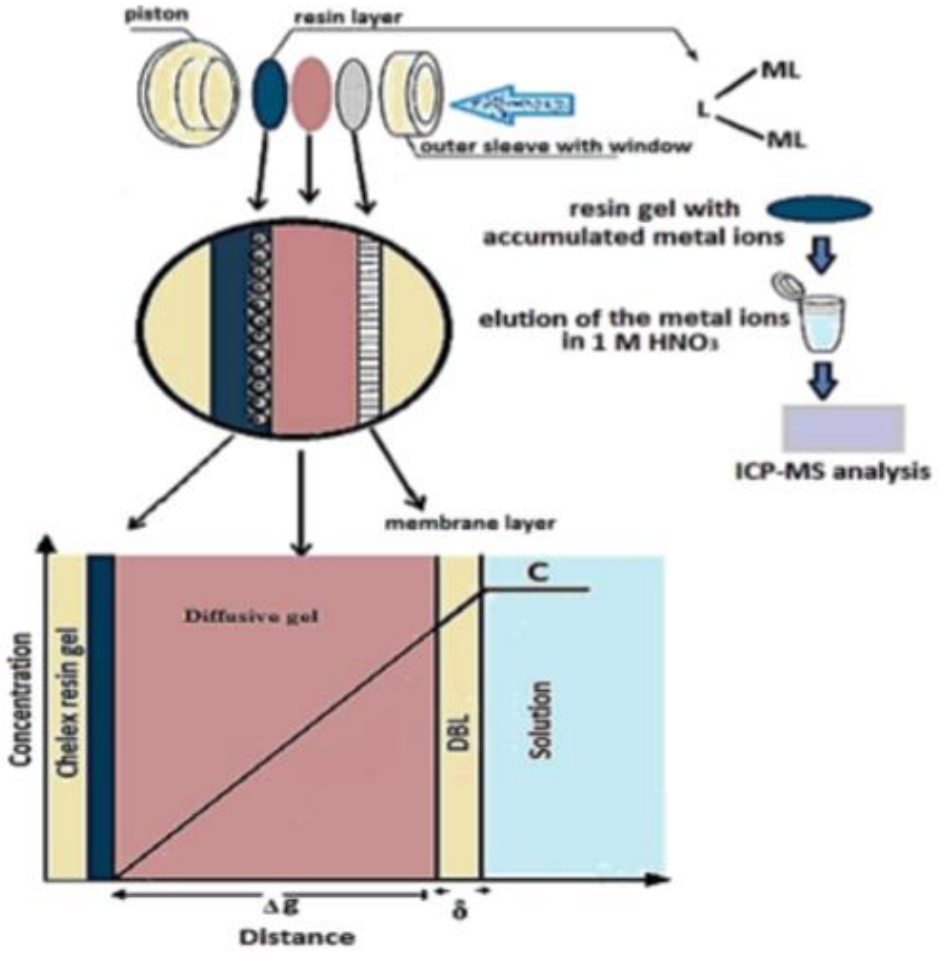


Figure 2-2: Modified cross-section of DGT components and the elution of accumulated metals from Chelex-100 resin

2.6.3 *DGT principle in soils*

DGT can be used in soils directly to give an insight into soil processes as it allows accumulation of metals in a well-defined geometry that thus permit the quantification of metal resupply from the solid phase (Zhang et al., 1998).

The DGT device perturbs the soil in a controlled way thereby introducing an in-situ local sink for metal ions, resulting fluxes to the device are measured quantitatively

allowing assessment of resupply kinetics and in-situ labile concentrations (Hooda et al., 1999).

When metal ions are removed from soil solution by DGT, just as if the metals are removed from soil solution by biological uptake, it may be resupplied from the solid phase of the soil to the solution (Ernstberger et al., 2005). There will be a net flux from soil to solution induced by the depletion by DGT device and the processes induced by deployment of a DGT probe in a soil is depicted in Figure 2.3.

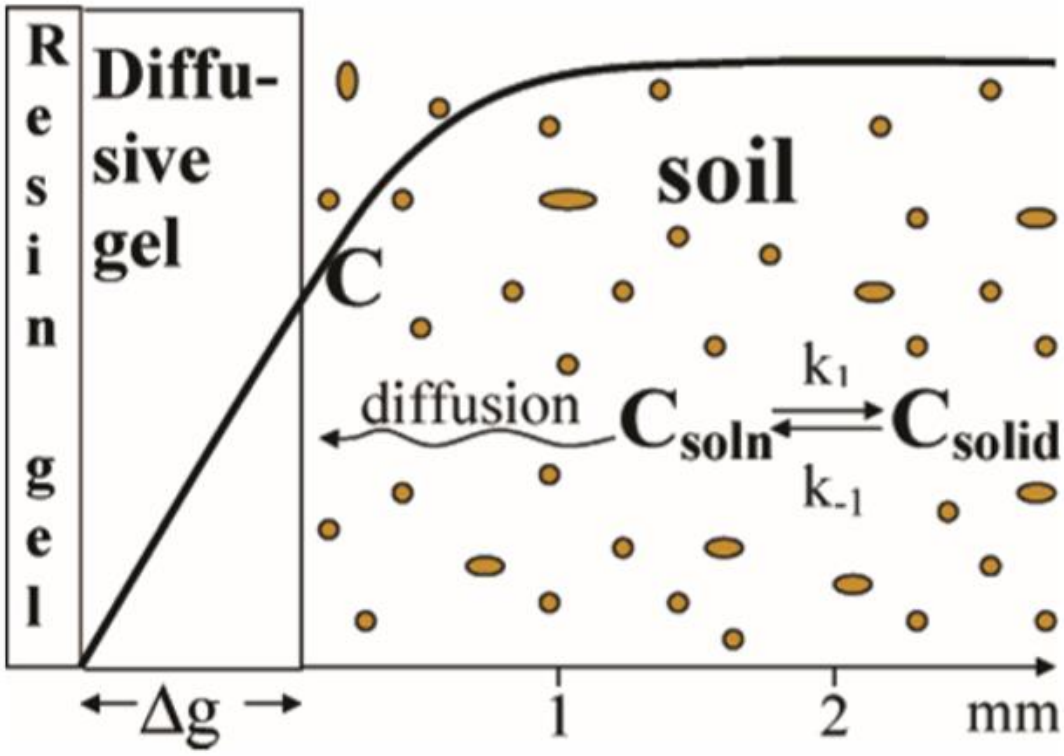


Figure 2-3: Processes induced by deployment of a DGT probe in a soil.

The DGT-induced soil to solution flux, (Fss), may be different from the potential maximum flux from soil to solution (Fpm); the DGT-induced soil to solution flux is referred to as a partial flux because it will just be a fraction of the potential maximum flux from soil to solution. The flux measured directly by DGT relates to the partial

flux and potential flux of metal ions from soil to solution in one of three possible ways depicted in Figure 2.4.

i. Fully sustained state: this is obtained when the ions removed by the DGT devices are rapidly resupplied from the soil solid phase and the concentration in solution is effectively buffered into a constant value.

ii. Unsustained state: implies that there is no resupply from the solid phase to the solution. Diffusion is the only mechanism responsible for the supply of ions from the soil solution to the DGT device. The soil solution concentration become gradually depleted first in the area surrounding the DGT device and then extends into the soil solution. In this case, the DGT flux declines with deployment time, although the initial concentration in solution can be calculated from the DGT measured mass.

iii. Partially sustained state: The resupply from the soil to solution in this case is not enough to sustain the initial bulk concentration and to satisfy fully the DGT demands. Which depends on the thickness of the diffusive gel layer and the initial metal concentration in soil solution. The fully sustained state may become partially sustained if the gel layer becomes thinner and the DGT demand become greater.

If the DGT measured concentration (C_{DGT}) is close to the soil solution concentration (Csoln), it is the fully sustained case. If the C_{DGT} is significant less than the Csoln, the soil solution is partially sustained. If the C_{DGT} is less than 10% of Csoln, it is unsustained case. There is no resupply from solid phase to soil solution. The flux can only be accounted for by simple diffusion.

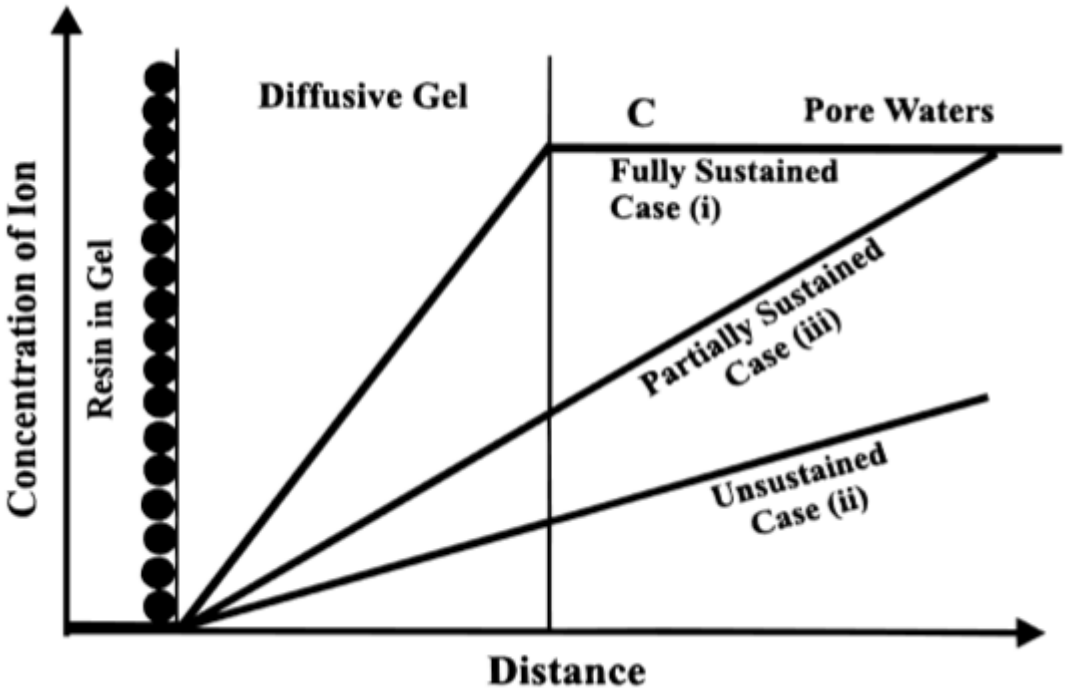


Figure 2-4: Schematic representation of the concentration gradient in a DGT assembly in contact with pore waters where the concentration is fully sustained (case i), partially sustained (case iii), unsustained (case ii) by resupply from the solid phase in soil.

2.7 Biochar in Soil Remediation

Lehmann and Joseph (2015) defined biochar as a porous substance that is produced by subjecting the carbon rich biomass to thermal decomposition in limited supply of oxygen and a relatively low temperature less than 700^{o}C (Mesa and Spokas, 2011).

Biochar derived from wood materials with high lignin contents is considered an effective remediation tool for soils for these basic reasons:

(1) it has the ability to hold and adsorb organic compounds and metals thus preventing their contacts with humans, animals and plants;

(2) it is able to enhance systemic resistance of plants to diseases and improves the introduction of beneficial microbes which in turn also promote remediation;

(3) it leads to improvement of soil quality and thus increased plant productivity.

The physical properties of biochar provide many benefits to the soils which makes it ideal for remediation and improving the ecosystem health, and also help to improve soil quality. Its bulk density is much lower than that of mineral soils (Brady and Weil, 2004). Biochar has a greater porosity compared to other types of soil organic matter and can thereby improve soil texture and aggregation thus improving water retention in the soil.

High pH value: Most biochar are alkaline materials with liming effect on soil and help in reducing the mobility of heavy metals in contaminated soils (Sheng et al., 2005). High Cation Exchange Capacity, (CEC): Generally, biochar has a high CEC. Thus, increasing its potential as a binding agent of organic matter and minerals: (Utomo et al., 2011). High adsorption capacity, high carbon content, high mechanical strength, high organic content, high nutrient retention capacity, high pesticides retention capacity and very long half-life (> 100 years) are some of the additional properties possessed by biochar. It has been revealed that the application of biochar may increase the overall net surface area of the soil (Chan and Xu, 2009).

2.7.1 *The mechanism of heavy metal stabilization by Biochar*

The incorporation of biochar to soils increase the negative charge on the soil surface due to the decreasing zeta potential and increasing CEC (Peng et al., 2011). This increase the electrostatic attraction between the positively charged heavy metal and soil.

A high soil pH value as a result of adding biochar may lead to decrease mobilization of heavy metals and thus encourages precipitation. Other complex mechanisms may also be obtainable during the interaction of biochar with heavy metals because there

are many different functional groups in the surface of the biochar, the formation of complexes between biochar and heavy metal could thus be an alternative route. The mechanism of heavy metal removal with biochar amendment might be explained through electrostatic interaction, precipitation and other complex reactions (Lu et al., 2012, Peng et al., 2011).

A study was conducted by Uchimiya et al. (2011) to fingerprint the principal components responsible for the stabilization of heavy metals (Cu, Ni, Cd, Pb) in soils. It was revealed that surface ligands like oxygen containing carboxyl, hydroxyl, and phenolic surface functional groups of soil organic and mineral components play central roles in binding metal ions, and amendment with biochar can be a means of increasing these surface ligands in soil.

An examination of an alkaline, clay San Joaquin soil polluted with metals showed that copper retention was enhanced by biochar and likely followed the electrostatic interactions between copper and negatively charged soil and biochar surfaces, sorption on mineral (ash) components, complexation of copper by surface functional groups and delocalized pi electrons of carbonaceous materials and precipitation.

It was discovered that increase in pH as a result of addition of basic biochar improved the immobilization of heavy metals. This led to a nonstoichiometric release of protons, suggesting that with higher carbonized fractions and chars' addition, heavy metal immobilization by cation exchange becomes increasingly outweighed by other controlling factors like the coordination by pi electrons of carbon-carbon double bonds and precipitation. In weathered acidic soil, the stabilization ability of biochar for heavy metals especially Pb and Cu, was directly linked with the amount of oxygen functional groups.

2.7.2 *Biochar reduces heavy metals concentrations*

Biochar is well suited for treating soils contaminated with heavy metals because it has shown to be very effective in adsorbing and sequestering a number of heavy metals and trace elements like arsenic, copper, lead, mercury, nickel, cadmium and chromium (Wingate et al., 2008). Biochar reduces the exposure potentials to animals or humans. By decreasing phytotoxicity, it allows soils that were at a time polluted to support diverse and healthy vegetation, this is very important for a balanced ecosystem.

A number of researchers have studied the effect of biochar on heavy metals in soils. The studies quantified the positive effects of biochar on reducing concentrations and bioavailability of heavy metals. Beesley et al. (2010) determined that biochar applied to soils resulted in a 10-fold decrease in Cd in the soil and a resultant reduction in phytotoxicity to plants.

The effect of biochar on the bioavailability and phytotoxicity of cadmium, copper and lead from contaminated soils was examined by Park et al. (2011). The result revealed that application of biochar significantly reduced NH_4NO_3 extractable Cd, Cu and Pb concentrations of soils, indicating the immobilization of these metals. A study in a rice paddy contaminated by a metallurgy plant showed that biochar reduced soil concentrations of Cd by an average of 35% and reduced rice plant uptake of Cd by an average of 37% (Cui et al., 2011).

2.8 Brief Description and Botanical Classification of *Delonix regia*

The flame of the forest which grows from 20 to 40 feet high is a medium sized tree with crooked trunks, irregularly twisted branches, and rough grey bark. Its worst appearance is in December and January when it has lost most of its leaves; but it

becomes a true tree of flame from January to March when it is seen in its most beautiful form with a root of orange and vermilion flowers covering the whole crown.

The flame of the forest also referred to as Royal Poinciana which is shown in Figure 2.5 requires tropical or a near tropical climate to flourish but it can endure salty and drought conditions (Roy et al., 2008).

(a)

(b)

Figure 2-5: Photograph of (a) *Delonix regia* tree; (b) *Delonix regia* pods

It is very widely grown in Africa and Hong Kong. The tree's vivid red/orange/yellow flowers and bright green foliage make it an exceptionally striking sight. It is grown for its ornamental value and it is also a useful shade tree in tropical conditions because it

grows to a modest height and spread widely, and its dense foliage provides full shade. The seeds pods are dark brown and can be up to 60cm in length and 5cm wide, the individual seeds, however, are small weighing an average of around 0.4g. The compound leaves have feathery appearance and a characteristic light, bright green colour. *Delonix regia* is a specie of flowering plant from the fabaceae family; noted for its fern-like leaves and flamboyant display of flowers (Cowen, 1984), its botanical classification is shown in Table 2.4 .

Table 2-4 Botanical Classification of *Delonix regia*

Kingdom	Plantae	Plants
Sub kingdom	Tracheobionta	Vascular plant
Super division	Spermatophyta	Seed plant
Division	Magnoliophy	Flowering plant
Class	Magnoliopsida	Dicotyledon
Sub Class	Rosidae	
Order	Fabales	
Family	Fabaceae	Pea family
Genus	*Delonix*	
Species	*Delonix regia*	

In 2011, (Rahman et al.) reported that the methanolic extract from the leaf of Delonix regia has glucose lowering capacity and that some folks in Bangladesh were using it to treat diabetes, this was supported in a recent review by Modi et al. (2016) where

various medicinal uses of different parts of the flame of forest tree were highlighted, it was only the pods that did not have any use in local medicine.

Though not much research had been done utilising the pods of the tree, some of the few available ones reported on the ability of activated carbon derived from the pods in removal of methylene blue dyes (Vargas et al., 2011) and certain heavy metals like mercury, cadmium (Festus et al., 2013, Okoronkwo et al., 2013, Shabudeen et al., 2013). Proximate, elemental and biochemical analysis of *Delonix regia* was done by Sugumaran et al. (2012) where the pods have the properties listed in Table 2.5.

Table 2-5: Proximate, elemental and biochemical analysis of *Delonix regia* pods (Sugumaran et al., 2012)

Parameters	**(%weight) dry basis**
Proximate Analysis	
Ash	2.80±0.65
Fixed carbon	5.20±3.81
Volatile matter	92.03±3.74
Elemental Analysis	
Carbon	34.22
Hydrogen	4.50
Nitrogen	1.94
Sulphur	0.42
Oxygen	58.91
Biochemical Properties	
Cellulose	13.90
Hemi-cellulose	24.13
Lignin	23.36

2.9 Rationale and Objectives of this work

Environmental pollution is a great concern for the whole world, but it is a more prominent problem in the Third World Countries such as Nigeria. Nigeria has majorly

depended heavily on Crude oil exploration to sustain its economy since 1956 and the series of exploration activities in the production area, Niger Delta part of Nigeria, has led to serious pollution of all spheres of the environment by both organic and inorganic pollutants. Local citizens in the production areas are experiencing great hardship because their major means of livelihood which are farming, and fishing have been lost to pollution and this has resulted in frequent cases of civil unrest in this area of the country (Agbaeze et al., 2015).

A solution to these incessant civil unrests is to solve the problem caused by environmental pollution in the area. The Nigerian government through various national organisations is spending huge amounts of money in reclaiming the polluted farmlands and searching for possible solutions to the pollution problems.

Solving the problems by innovative and affordable technologies is the major goal for the government and scholars are being sponsored to investigate on different remediation methods that will be practical under the prevailing economic conditions in Nigeria. Adsorption with activated carbon had been used for the removal of heavy metals from water for quite a long time, since 1927 (Netzer and Hughes, 1984), but the high cost of the commercial activated carbon (Babel and Kurniawan, 2003) and its importation to Nigeria will hamper its use in wastewater treatment. Different types of low cost adsorbents with various capacities have been investigated but there is need to explore some new materials in a bid to find the one that will be most suitable for the removal of heavy metals.

Delonix regia was choosen as the adsorbent to explore in this study because it is a widely available waste in Nigeria. The objectives of this work are listed as following:

(a) investigate the effects of basic operating conditions, such as the pH, contact or shaking time, initial metal concentrations, different ionic strength, on the adsorption of heavy metals; determine the adsorptive capacities of *Delonix regia*; investigate recovery capabilities of the bound metals from the spent biomass;

(b) establish the kinetic and isothermal parameters of the process;

(c) investigate the effectiveness of using *Delonix regia* material for soil remediation and establish a holistic programme of using DGT as a method to assess risk pre- and post- remediation;

(d) determine labile pool size and kinetic parameters of heavy metals in soils using DGT and DIFS model.

Chapter 3. Investigating Adsorptive Capacity of *Delonix regia* Pods for The Removal of Heavy Metals from Waste Water

3.1 Introduction

An issue requiring serious attention worldwide is the pollution resulting from heavy metals because heavy metals are persistence in nature (Fu and Wang, 2011), toxic on living organisms and have adverse effects on the environment (Chronopoulos et al., 1997). Mercury, cadmium, lead, nickel, cobalt, chromium and copper are few of the heavy metal ions that are great danger to human health (Bailey et al., 1999). These heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders (Bulut and Zeki, 2007).

Pollution by heavy metals started ages back when ore processing began by human (Renberg et al., 1994), heavy metals are released into the environment through a wide range of processes and activities such as combustion, extraction and processing (Järup, 2003). They are able to gain access into the environment and cause pollution through many anthropogenic sources of which some are agricultural activities during the application of fertilizers, fungicides and pesticides; metal smelting, welding, electroplating, battery manufacture, nuclear fission plants, mining, textile making, operations in tannery industries, paints manufacture and usage, burning of coal, fuel production in refineries, automobile emission and manufacture of brass (Paul, 2017) and also as a result of discharge of municipal wastes and effluents from industries like electronics manufacturing (Wang et al., 2013b).

Removal of heavy metals from industrial wastewater, the major source of discharge to the environment, have involved several methods which are either expensive or ineffective with large effluent volumes (D'Avila et al., 1992, Kapoor and

Viraraghavan, 1995, Wilde and Benemann, 1993) and furthermore some of these conventional methods generate toxic sludges which become another environmental issue (Sandau et al., 1996). Adsorption with activated carbon is considered the best technology because of its excellent adsorption ability and has gained acceptance as an alternative treatment method (Alslaibi et al., 2013, Kurniawan et al., 2006). However, its use is highly cost intensive especially for developing countries of the world and its use has been greatly restricted because of this.

In view of these, it is very important to find cheaper and eco-friendly means of removing metals from industrial wastewater which is a major source of pollution. Research is being conducted in search of materials from agricultural and biological origin as adsorbents (Pino et al., 2006a, Pino et al., 2006b) because these materials are always available in large volumes, they have very low or no commercial value, are easily degraded by micro-organisms and in most cases there is no storage facilities for them in developing countries. At the best, all they are used for is animal feeds or disposal in landfill causing another environmental issue. These agricultural wastes containing a high quantity of lignin, hemicellulose, cellulose and certain proteins. They should constitute an inexpensive, eco-friendly renewable natural resources if their potentials are explored. However, most of these researches are focussed on using these agro-waste as precursors for activated carbon (derived from plants wastes) and in most cases the purpose of the study (a cheaper alternative to activated carbon) is more or less defeated, because the cost of energy needed to obtain the high temperatures of over 900^{o}C required for producing activated carbon is an additional cost and will be burdensome or more or less unachievable for the emerging small scale industries we have in the developing parts of the world where power supply is very erratic.

In this work, the natural, unmodified powder from the pods of *Delonix regia* was used for the adsorption of Lead, Nickel, Copper, Cadmium and Cobalt from synthetic waste water under different experimental conditions.

The aim of this work is thus to investigate the adsorption characteristics of Flame of the forest (*Delonix regia*) pods for the removal of metals such as Lead, Cadmium, Copper, Cobalt and Nickel ions from aqueous solutions and investigate the potential of using *Delonix regia* for remediating contaminated waters.

In order to achieve the aim of this work, the following objectives were set:

(a) investigate the effects of operating conditions such as the pH, ionic strength, contact time and initial metal concentration;

(b) investigate recovery capabilities of the bound metals from the spent biomass;

(c) establish the kinetic and isothermal parameters of the adsorption process.

3.2 Materials and Methods

3.2.1 *Materials*

Delonix regia pods were used as the adsorbents for adsorption experiments in this chapter and the leaves were used for the next chapter.

Lead trioxonitrate (V), Copper chloride dihydrate, Cobalt sulphate heptahydrate, Diammonium nickel sulphate hexahydrate and Cadmium nitrate salts were used for the preparation of 1000 ppm stock Pb(II), Cu(II), Co(II), Ni(II) and Cd(II) solutions respectively by dissolving the salts in high purity Milli-Q water.

Nitric acid (0.1M) and sodium hydroxide solutions were used for the adjustment of pH where it was necessary; Sodium nitrate was used for ionic strength study and 0, 0.1, 0.5 and 1M nitric acid were used for the desorption of adsorbed metal from the used biomass.

3.2.2 *Methods*

3.2.2.1 Biomass Preparation

The matured dried pods of the biomass, *Delonix regia* were harvested in The Ekiti State University, Ado Ekiti, Nigeria. The dried pods were split open in order to remove the seeds, afterwards the pods were sun dried and chopped into small pieces.

The small pieces were thoroughly washed with MQ water and oven dried at 100^{o}C-105^{o}C for 3 days; after which it was milled into powdered form using a Tema milling machine. The powder was sieved through 250µm mesh nylon sieve and kept in air tight containers for further experiments.

3.2.2.2 The effect of pH

Determination of the optimum pH for adsorption is paramount to the success of further investigation. From the prepared biomass, 0.5g was weighed into designated tubes containing 20mls of 100 ppm of the metal solution of various pH between 1.0 to 8.0. The different pH values were obtained by using 0.1M HNO_3 and 0.1M NaOH solutions. The suspensions were shaken for 5 hours at room temperature (21±2^{o}C) and this experiment was completed by carrying out the processes in section 3.2.2.9. After determining the best pH for each metal adsorption, subsequent studies were conducted at this pH value.

3.2.2.3 The effect of interaction time

Batch experiments to determine the optimum interaction time of the *Delonix regia* biomass to adsorb the metals were carried out at 21±2^{o}C. Adjustment to the optimum pH (of 4 for lead, copper and cobalt; 5 for nickel and 6 for cadmium) for the sorption was done for 100ppm of metals solutions, then 0.5g of the prepared biomass was poured into the designated tubes (1 to 9) containing 20mls of 100ppm of the metal solution. Contacting and continuous shaking was done for 0.5 mins, 1 min, 3 mins, 5 mins, 15 mins, 30 mins, 60 mins, 90 mins, 120 mins, 180 mins, 240 mins and 300 mins and after the time lapse, after the time lapse procedures in section 3.2.2.9 was done to complete sample analysis. Having determined the optimum interaction time, further investigations were conducted at the optimum pH and contact time.

3.2.2.4 Experiment for Sorption Isotherm Modelling

Various concentrations of the adsorbate in the range of 1 ppm, 5, 10, 20, 50, 100, 200, 500,1000 ppm were used for the adsorption experiment in order to obtain the data to generate the adsorption isotherm for the understanding of the adsorption process. Adjustment to the optimum pH (of 4 for lead, copper and cobalt; 5 for nickel and 6 for cadmium) was done for the different concentrations of each of the metal solutions. The desired weight of 0.5g of the prepared biomass was added to designated tubes containing 20mls of the desired concentration of the metal solutions and shaken continuously for 30 minutes. The procedure was repeated for each of the concentrations listed above and at the expiration of contact time, the procedure in section 3.2.2.9 was carried out for sample analysis.

3.2.2.5 The effect of ionic strength

In order to study the influence of the presence of other ions in solution on the uptake of metal ions, sodium nitrate was used as ionic medium. Different concentrations (0.001, 0.005, 0.01, 0.05, 0.1, 0.5M) of the salt was prepared. From each of these concentrations 100ppm of each metal solution was prepared, the pH was adjusted as necessary and mixed on a shaker for two hours then 20mls were measured into designated tubes already containing 0.5g of the prepared biomass. Shaking was done for the duration of 30 minutes, the complete procedure involved for sample analysis is explained in section 3.2.2.9.

3.2.2.6 Biosorbent Dose Study

Optimum amount of biosorbent was determined by using different doses (0.25, 0.5, 0.75, and 1.0g) in 100ppm of metal solution after adjustment to the optimum pH (of 4 for lead, copper and cobalt; 5 for nickel and 6 for cadmium). Each biomass dose and 20mls metal solution of adjusted pH were shaken for 30 minutes after which the process outlined in section 3.2.2.9 was carried out.

3.2.2.7 Recovery or Desorption experiments

Recovery of the metal ions from the biomass was carried out with different concentrations (0, 0.05, 0.1, 0.5, and 1.0 M) nitric acid. The desired volume of 20mls of 100ppm of metal solution of adjusted pH was poured into designated plastic tubes for each concentration of desorbing agent. These metal solutions were mixed with 0.5g of the biomass for 30 minutes after which they were centrifuged twice at

4500rpm for 15 minutes and 10300rpm for 10 minutes, the supernatant or liquid part was discarded, and the biomass were then mixed with 20mls of the appropriate concentration of the desorbing agent (HNO_3) for another 30 minutes. The process analysis is completed in section 3.2.2.9.

3.2.2.8 Experimental adsorption capacity

A volume of 1000mls of 200ppm metal solution was adjusted to the optimum pH (of 4 for lead, copper and cobalt; 5 for nickel and 6 for cadmium) out of which 20mls was poured into a plastic tube containing 0.5g of the prepared biomass. The suspensions were shaken for 30 minutes, centrifuged at 4500rpm for 15 minutes and transferred into clean tubes before 100µls of the samples were withdrawn and diluted a thousand times with 0.1M HNO_3 for metal content analysis, this was regarded as the first cycle. The solid phase retained on the filter paper was washed back into their respective tubes with a fresh 20mls, 200ppm of the metal solutions of adjusted pH and shaken for 30 minutes. The suspensions were centrifuged at 4500rpm for 15 minutes, filtered into clean tubes for dilution and subsequent metal analysis, this was referred to as the second cycle. The procedure of mixing with fresh metal solution, centrifugation and filtration was repeated for a minimum of six times and each step is referred to as a cycle and at the end of all the cycles sample analysis in section 3.2.2.9 was done.

3.2.2.9 Sample Analysis

Prior to the analysis of the samples with the ICP-MS, sample suspensions were centrifuged twice at 4500rpm for 15 minutes and 10300rpm for 10 minutes, then 100µls of the supernatant were withdrawn, diluted a thousand times with 0.1M HNO_3.

After the dilution of samples then 20 ul of 50 ppb of internal standard solution (containing Rhodium) was added to all the samples and the calibration standards used for metal analysis and mixed properly.

Multi-elements standard solution was used to prepare different concentrations of (1, 5, 10, 20, 50 and 100ppb) external calibration standard solutions used for each analysis.

The analysis of the samples was done with Thermo Elemental Inductively Coupled Plasma-Mass Spectrometer (X Series II). After the instrument is switched to the operate mode, the pressure of the nebulizer was checked, and the instrument's sensitivity and stability was checked by running a tuning solution of 1ppb multi element standard solution for 10 minutes. It was ensured that the ^{115}In counts was less than 20K counts per second, precision less than 2%. The Backgrounds (5BKg and 220BKg) were less than 1 count per second, the oxides Cerium oxide (CeO^{+}) must be less than 2.0% and the doubly charged ions (Ba^{2+}) less than 6.0%.

Then the calibration standard solution inclusive of a blank and 0ppb solutions are analysed in order to obtain a calibration curve where the samples to be analysed will properly fit into. Once the calibration curve for each metal is good with $R^2 = 0.999$, analysis of the samples can proceed.

3.2.2.10 Quantification of adsorption

The concentration of unadsorbed metal ions in the sorption medium was determined by ICP-MS (X Series II). Each experiment was repeated three times, each measurement was repeated three times and the results are the average values after correction was made for the experimental blanks.

The amount of metal ions (^{208}Pb, ^{60}Ni, ^{65}Cu, ^{111}Cd and ^{59}Co) adsorbed on *Delonix regia* (Qe in mg/g) was calculated using equation 3.1 below:

$$Qe = (Ci - Ce)V/m \quad \text{..... Equation 3-1}$$

where Ci is the initial metal concentration in solution (mg/l),

Ce is the final metal concentration in the solution (mg/l),

V is the volume of the metal solution used in litre (L) and

m is the mass of the biosorbent (g).

3.3 Results and Discussion

3.3.1 *Effect of pH*

The pH of the solution is an important factor in the adsorption experiment as it affects the surface functional group of the biomass and the solubility of ions in aqueous solutions. At low pH values hydrogen ions tends to occupy the binding sites, this increases the repulsive forces needed to be overcome by the metal before binding can take place and consequently make it more difficult for the metal ions to access binding sites (Saeed et al., 2002) and thus a lower uptake is observed. The result of pH effect on the uptake of Pb, Ni, Cu, Cd and Co ions from solutions by *Delonix regia* biomass is shown in Figure 3.1.

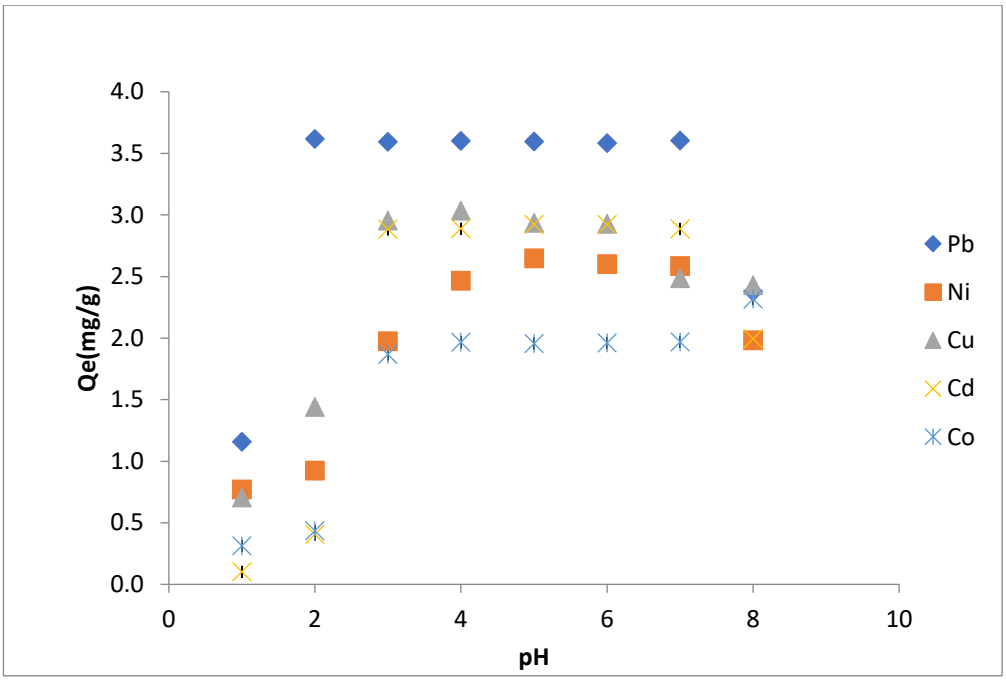


Figure 3-1:The effect of pH on the adsorption of Pb, Ni, Cu, Cd and Co by *Delonix regia* pods{pH: 1-8; contact time: 300mins; metal ions concentration:100ppm; adsorbate volume:20mls; biosorbent dose: 0.5g, shaking rate:18 rpm; temp:21^{o}C ±2}.

It revealed that there was a noticeable increase from pH 1 to 2 after which the values were more or less constant. pH 4 was chosen as the optimum for lead because the uptake of lead doesn't seem to be affected much by the pH of the solution after pH 4. The effect of pH on the uptake for nickel showed that there was no significant sorption at low pH values but increase sorption was recorded as pH increased showing the sorption to be dependent on pH of the solution. pH 5 was used for nickel in subsequent experiments. A high increase in sorption with uptake value from 0.71 to 2.9mg/g was recorded at low pH (1-3) values for copper, at pH 4 a maximum uptake was achieved and pH 4 was used as the optimum pH for copper in other experiments.

For cadmium, very low sorption was observed at pH 1 and 2; this increased at pH 3 and remained fairly constant from pH 4 to 8. pH 6 was used as the optimum for all

other cadmium experiments. For cobalt ions, the sorption is gradually increased until a maximum uptake was reached at pH 4 after which the uptake was constant until pH 7.

The results obtained for all the metals showed that the sorption is highly dependent on pH and this is in conformity with the work done by Xue et al. (2009) when the adsorption of Pb, Cu, Cd and Zn on to furnace slag was investigated . It was reported by Bulut and Zeki (2007) that significant increase in the sorption of Pb(II) ion on wheat bran was observed in the pH range from about 4 to 7. An optimum pH of 6 was reported for the sorption of nickel onto a fungus, *Rhizopus nigricans,* by Volesky and Holan (1995).

Although pH 4 to 6 were used as the optimum pH for this study, but from the result in Figure 3.1, it was revealed that the pods of *Delonix regia* has significant uptake for all the metals considered at pH 3. This result showed a potential in this adsorbent because some heavy metal bearing effluents have pH values which could be as low as 2 (Andrade et al., 2017, Cavaco et al., 2007, Vergili et al., 2017) using this adsorbent on such effluent could be promised to yield a good sorption because even at low pH values used in this study, the performance of the adsorbent for the targeted heavy metals was above 70%, thus using this adsorbent will reduce the necessary cost for pH adjustment before wastewater treatment. Table 3.1 shows researches with similar optimum pH values to the present work.

Table 3-1: Optimum pH values in heavy metals-agricultural wastes adsorption systems

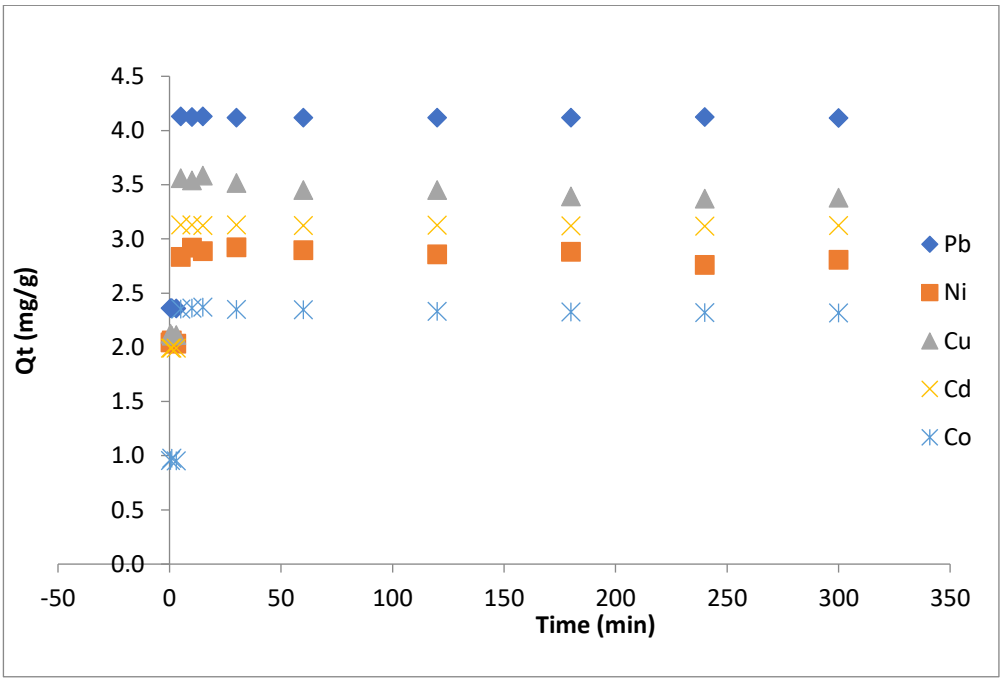
Metal ions	Adsorbent	Optimum pH	References
Pb(II)	Portulaca plant mass	6.0	(Dubey and Shiwani, 2012)
	Pineapple peel fibre	5.6	(Hu et al., 2011)
	Cocoa pod husk	6.0	(Njoku et al., 2011)
	Pine cone powder	5.0	(Ofomaja et al., 2010)
	Onion skins	6.0	(Saka et al., 2011)
Ni(II)	Orange peels	5.0	(Gönen and Serin, 2012)
	Rice bran	6.0	(Zafar et al., 2007)
	Cashew nut shell	5.0	(Senthil Kumar et al., 2012)
	Moringa oleifera bark	6.0	(Reddy et al., 2011)
	Caesalpinia bonducella seed	5.0	(Gutha et al., 2011)
Cu(II)	Garden grass	6.0	(Hossain et al., 2012b)
	Pineapple peel fibre	5.4	(Hu et al., 2011)
	Soybean meal waste	5.0	(Witek-Krowiak and Reddy, 2013)
	Cashew nut shell	5.0	(SenthilKumar et al., 2011)
Cd(II)	Wheat straw	6.0	(Farooq et al., 2011)

	Potato peel	6.0	(Taha et al., 2011)
	Castor seed hull	6.0	(Sen et al., 2010)
	Various mushroom	6.0	(Vimala and Das, 2009)
	Cashew nut shell	5.0	(Senthil Kumar et al., 2012)

3.3.2 *Effect of interaction time*

Time of interaction carried out in the study of the adsorption is very important for industrial application. An ideal biosorbent should rapidly adsorb the metal ions in the first few minutes of interaction with the solutions; this is evident from the result of the study conducted using *Delonix regia* biomass. Rapid uptake of the metals by the biosorbent is desirable providing for a short solution-biosorbent contact time in the actual process (Volesky, 1990). The result obtained from the interaction time study is represented in Figure 3.2.

(a)



(b)

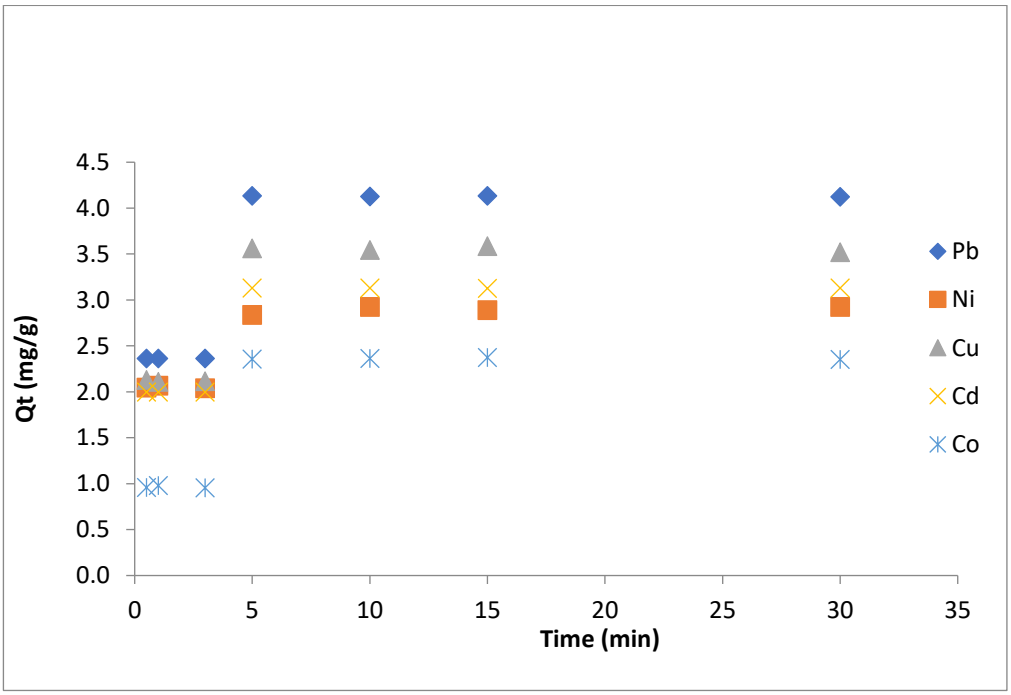


Figure 3-2: The effect of interaction time on the adsorption of Pb, Ni, Cu, Cd and Co by *Delonix regia* pods pH: 4-6; contact time:0.5-300mins; metal ions concentration:100ppm; adsorbate volume:20mls; biosorbent dose: 0.5g, shaking rate:18rpm; temp:21^{o}C ±2}

The result shown in Figure 3.2 revealed that adsorption of the lead, nickel, copper, cadmium and cobalt ions on to *Delonix regia* biomass was very rapid as significant uptakes of about 80% sorption which is equivalent to 4.0mg/g was achieved for lead; 2.9mg/g, 3.6, 3.1 and 2.4mg/g was recorded for nickel, copper, cadmium and cobalt respectively within the first fifteen minutes of contacting the biomass with the metal ions solutions. The quick sorption of the metal ions suggests that chemical sorption rather than physical sorption contributes to their sorption onto *Delonix regia*. But after the first fifteen minutes of interaction the sorption uptake was relatively the same over the period of 300 minutes that was investigated. Experimental time of 30 minutes at which the uptake values of (4.1mg/g, 2.9mg/g, 3.5mg/g, 3.1mg/g, 2.4mg/g) was observed for lead, nickel, copper, cadmium and cobalt respectively was chosen as the experimental contact time for all other experiments. After 30 minutes, the rate of uptake became constant for the remaining duration of 300 minutes carried out in this study. A contact time of 30 minutes was thus used for subsequent experiments. The fast uptake of metal by *D.regai* will be a cost effective advantage in industry as many batches of effluents could be treated within a short period of time.

Similar sorption rate was reported in studies with Cd, Fe and Pb removal by *Schizomeris leibleinii*, a green algae, (Özer et al., 1999). *Okieimen et al. (1988)* reported a maximum time of 20 minutes for Cd, Pb, Ni, Zn and Cu on modified cellulosic materials.

3.3.2.1 Kinetics Modelling

The kinetic modelling of experimental data, obtained from the time dependence study, shown in Figure 3.3 was carried out in order to predict the mechanism involved in the

sorption and determine the potential rate controlling steps such as external film diffusion, mass transfer and chemical sorption processes.

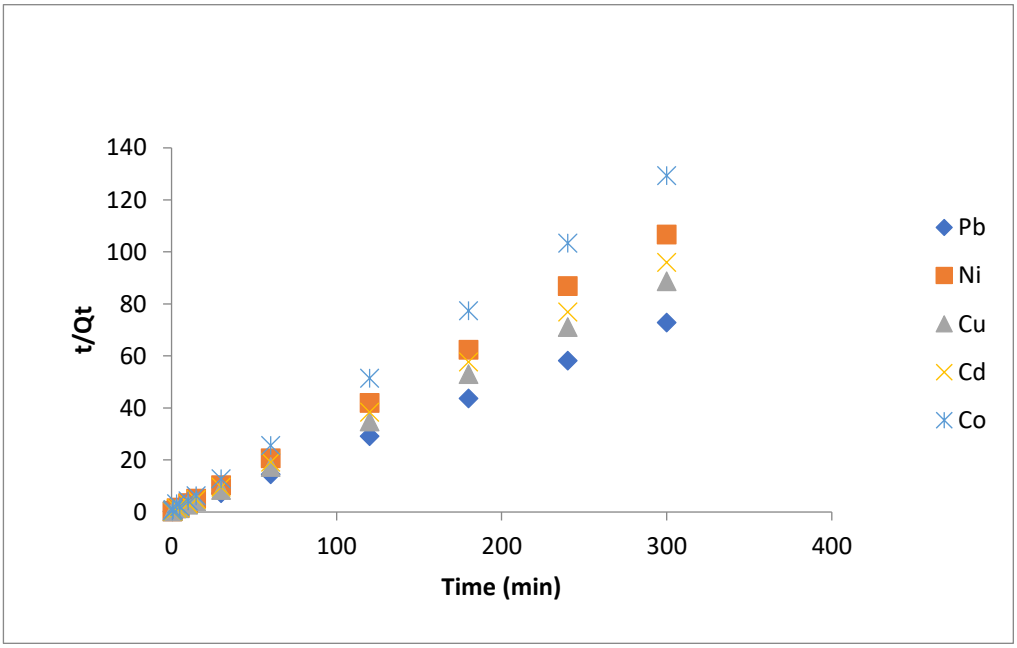


Figure 3-3: Pseudo-second order kinetics study of the adsorption of Pb, Ni, Cu, Cd and Co by *Delonix regia* pods {pH: 4-6; contact time:0.5-300mins; metal ions concentration:100ppm; adsorbate volume:20mls; biosorbent dose: 0.5g, shaking rate:18rpm; temp:21^{o}C ±2}

Kinetic models' equations assume that measured concentrations are equal to concentration or amount of adsorption sites and that in well agitated systems external film diffusion is negligible. The pseudo second-order equations which are based on the sorption capacity of the solid phase are used in this study. The data were fitted to the pseudo second order with the advantage of being able to predict the behaviour over the whole range of adsorption and is in agreement with chemical sorption mechanism being the rate controlling step (Ahmad et al., 2018, Aksu, 2001).

A pseudo-second order kinetic model expressed by equations (3.2 to 3.5) were used to simulate the kinetic sorption process in order to obtain the specific rate constant of the process.

$$\frac{dQ_t}{dt} = k_{2,ad}\left(Q_{eq} - Q_t\right)^2 \quad \text{.....Equation 3-2}$$

where $k_{2,\ ad}$ is the rate constant of second-order adsorption (g mg^{-1} min^{-1}). For the boundary conditions t=0 to t=t and Q_t=0 to Q_t=Q_{eq}; the integrated form becomes

$$\frac{1}{(Q_{eq}-Q_t)} = \frac{1}{Q_{eq}} + k_{2ad} \quad \text{..... Equation 3-3}$$

which is the integrated rate law for a second-order reaction and can be rearranged to obtain

$$Q_t = \frac{t}{\frac{1}{\left(k_{2,ad}Q_{eq}{}^2\right)}} + \frac{t}{Q_{eq}} \quad \text{..... Equation 3-4}$$

which has a linear form

$$\frac{t}{Q_t} = \frac{1}{k_{2,ad}Q_{eq}{}^2} + \frac{1}{Q_{eq}t} \quad \text{.....Equation 3-5}$$

If second-order kinetics are applicable, the plot of t/Q_t against t should give a linear relationship, from which Q_{eq} and $k_{2,ad}$ can be determined from the slope and intercept of the plots (Ho and McKay, 1999a), where $k_{2,ad}$ (g.$mg^{-1}$$min^{-1}$) is the second order rate constant for the sorption, Q_{eq} and Q_t are the amount of biosorbent at equilibrium and at any time t, respectively (mg/g). The main assumption of pseudo second order kinetic model is that the rate limiting steps may be chemical sorption involving forces through exchange or sharing of electrons between the metal ions and the biomass (Al-Rub et al., 2002). From Figure 3.3 straight-line plots of t/Q_t vs. t indicate that the kinetic sorption of Pb, Ni, Cu, Cd and Co can be well described by the pseudo-second-

order rate equation. The values of $k_{2,ad}$ and Qe calculated from the intercept and slope of the equation is shown in Table 3.2. From Table 3.2 and Figure 3.3, it is evident that kinetic of sorption for lead, nickel, copper, cadmium and cobalt by *Delonix regia* has a high correlation coefficient of 0.999 and thus followed pseudo-second order kinetic model.

Table 3-2: Adsorption parameters obtained from the second order kinetic model for the sorption of metals to *Delonix regia* pods

Metal ions	k_2 **(g.mg^{-1}min^{-1})**	Q_e**(mg/g)**	R^2
Lead	-151.52	4.1	0.9998
Nickel	-2.36	2.8	0.9996
Copper	-3.24	3.4	0.9999
Cadmium	-86.96	3.1	0.9998
Cobalt	-5.74	2.3	0.9997

3.3.3 *Effect of initial metal concentration on adsorption*

The result of the effect of changing the initial concentration of the metal ions while keeping the adsorbent dose and other factors constant during the adsorption experiment are presented in Figure 3.4.

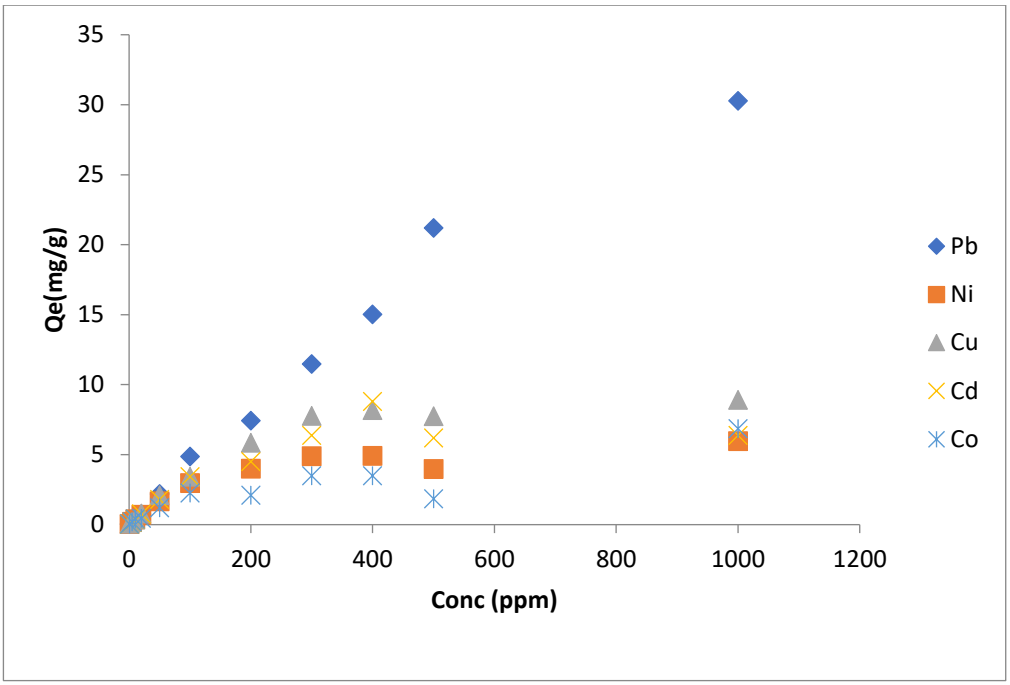


Figure 3-4: The effect of concentration on the adsorption of Pb, Ni, Cu, Cd and Co by *Delonix regia* pods {pH: 4-6; contact time: 30mins; metal ions concentration:1ppm - 1000ppm; adsorbate volume:20mls; biosorbent dose: 0.5g, shaking rate:18rpm; temp:21^{o}C ±2}

It showed that there was an increase in the uptake of the metal ions by *Delonix regia* as the concentration of the metal ions in solution was increased. The increase in uptake was linear for lead ion up to 500 ppm concentration, for nickel, copper and cadmium the linear increase was observed to 400 ppm. These indicate that at these concentrations the ions were able to interact very well with the binding sites available in the biomass. The increase in uptake with increasing concentration was due to more metal ions occupying the fixed number of active sites on the biomass surface. The uptake of Co ions increased linearly up to 100 ppm where an uptake value of 2.3 mg/g was recorded, increase in concentration to 200 ppm resulted in a decrease uptake of 2.1 mg/g. The difference in the uptake between lead and the other metals is probably due to its large electronegativity of 2.3 compared with other metals having 1.9, 1.9, 1.7 and 1.9 for nickel, copper, cadmium and cobalt respectively.

Some research carried out using different types of industrial effluents, reported the concentrations of Pb to be between 0.1-45.4 mg/l; Ni (0.8-4.7 mg/l); Cu (1.5-164.5 mg/l); Cd(0.1-76.1 mg/l); and Co (0.04-3.51 mg/l) (Akpomie and Dawodu, 2016, Basha et al., 2011, Bhateria and Dhaka, 2017, Noreen et al., 2017, Vaseem et al., 2017, Zhou et al., 2016), it thus implied that *Delonix regia* could be used to effectively remove each of these targeted metals from wastewater because the expected concentration in the wastewater is within the linear experimental concentration range.

3.3.3.1 Adsorption Isotherms Modelling

Adsorption isotherms express the relation between the amount of adsorbed metal ions per unit mass of biosorbent (Q_e) and the metal concentration in solution (C_e) at equilibrium. It can be generated based on numerous theoretical models where Langmuir and Freundlich models are used in this study (Carbonell, 1986, Langmuir, 1918). The adsorption model constants values give an expression of the surface properties and affinity of the adsorbents for the sorption of lead, nickel, copper, cadmium and cobalt ions. The Langmuir isotherm for the sorption shown in Figure 3.5 is a valid monolayer sorption on a surface containing a finite number of binding sites.

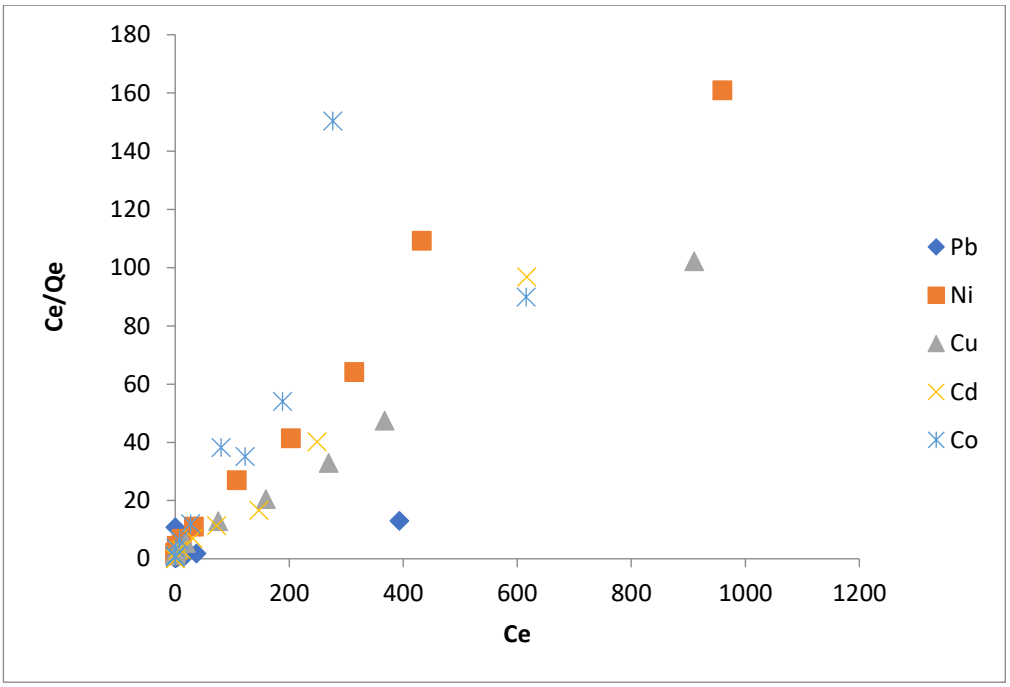


Figure 3-5: Plot of Langmuir Isotherm for the adsorption of Pb, Ni, Cu, Cd and Co by *Delonix regia* {pH: 4-6; contact time: 30mins; metal ions concentration: 1ppm - 1000ppm; adsorbate volume: 20mls; biosorbent dose: 0.5g, shaking rate: 18rpm; temp: 21°C ±2}

It assumes uniform energies of sorption on the surface and no transmigration of sorbate in the plane of the surface. The Langmuir equation may be written as shown in equations 3.6 and 3.7:

$$Q_e = \frac{Q^0 b C_e}{1+bC_e} \quad (non\ linear\ form) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 3-6}$$

$$\frac{C_e}{Q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \quad (linear\ form) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 3-7}$$

Where Q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e, the equilibrium concentration of solute in the bulk solution (mg/l), Q^0, the monolayer adsorption capacity (mg/g) and b is the constant related to the energy of adsorption. The effect of isotherm shape can be used to predict whether a sorption system is "favorable" or "unfavorable" both in fixed-bed systems (Weber and Chakravorti, 1974) as well as in batch processes (Poots et al., 1978). According to Hall et al.

(1966), the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R, expressed in equation 3.8, K_R is a dimensionless separation factor, C_i, the initial metal ion concentration (mg/L) and K_a is the Langmuir constant (L/mg). which is defined by the following relationship:

$$K_R = \frac{1}{1+ k_a C_i} \quad \text{.....Equation 3-8}$$

The parameter K_R indicates the shape of the isotherm accordingly:

When K_R =0 indicate an irreversible isotherm

0< K_R <1 indicate a favourable isotherm

K_R =1 it is a linear isotherm

K_R >1 the isotherm is termed unfavourable

The K_R values obtained for the sorption process shows that there is a favourable sorption of the metals unto *Delonix regia*. The adsorption capacity for each of the ions investigated is shown is Table 3.3, from the plots in Figure 3.5 it was observed that the sorption is favourable at initial concentrations below 200 ppm for all the metals except cobalt whose sorption is favoured at concentration below 100 ppm. The values of calculated adsorption capacity for each metal was close to the experimental values.

The Freundlich Isotherm, with plots shown in Figure 3.6, says the ratio of the amount of solute adsorbed onto a given mass of the sorbent to the concentration of the solute in the solution is not constant at different concentration. The non-linear and linear forms are shown in equations 3.9 and 3.10 respectively (Adebowale et al., 2006).

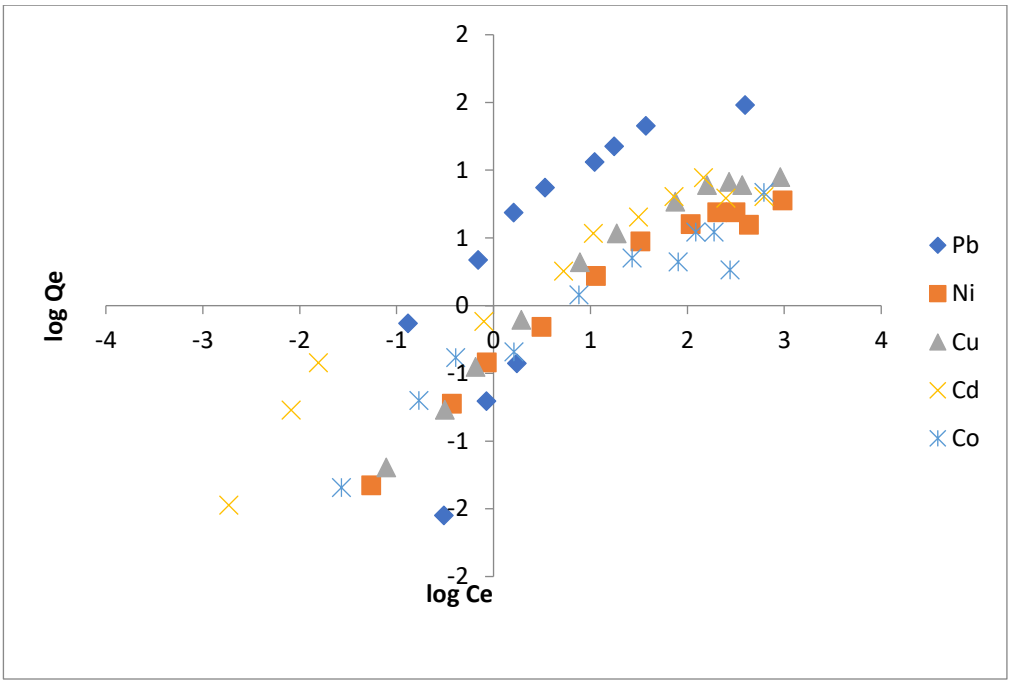


Figure 3-6: Plot of Freundlich Isotherm for the adsorption of Pb, Ni, Cu, Cd and Co by *Delonix regia* {pH: 4-6; contact time: 30mins; metal ions concentration:20ppm - 1000ppm; adsorbate volume:20mls; biosorbent dose: 0.5g, shaking rate:18rpm; temp:21^{o}C ±2}

$Q_{e} = K_F Ce^{1/n}$ …….. Equation 3-9.

$Log\ Q_e = Log\ K_F + \frac{1}{n} Log\ C_e$ ……. Equation 3-10

where: 1/n and K_F are constants related to adsorption efficiency and adsorption capacity respectively; Q_e is amount of adsorbate adsorbed per unit weight of adsorbent and Ce is the final metal concentration in the solution.

The adsorption intensity or efficiency, (1/n) for the Freundlich isotherm is a factor related to the surface heterogeneity and the multiplicity of the energies linked in the adsorption reaction, it also indicates a favourable sorption of the sorbate on the given sorbent.

1/n =0 indicate an irreversible isotherm

0<1/n<1 shows a favourable adsorption and

1/n >1 indicates an unfavourable isotherm (Areco et al., 2014).

The plots in Figure 3.6 is the Freundlich Isotherm model for the sorption of lead, nickel, copper, cadmium and cobalt by *Delonix regia* from where the values of the Freundlich constants shown in Table 3.3 were calculated. From the calculated 1/n values it showed that the Freundlich Isotherm is also favourable for the sorption of the metals. Considering the results obtained for the sorption processes it is seen that both isotherms can be adequately used to represent the sorption of these metals unto *Delonix regia* depending on the concentration of the adsorbate in solution. Langmiur isotherm is good at low concentrations while Freundlich is better over a wider concentration range except for the sorption of cobalt.

Table 3-3: Adsorption parameters of the Isotherm Models for the sorption of Pb, Ni, Cu, Cd and Co to *Delonix regia*

	Langmuir Isotherm				**Freundlich Isotherm**		
Metal ion	**Q_o (mg/g)**	**b (L/mg)**	**r^2**	**K_R**	**K_f (mg/g)**	**1/n**	**r^2**
Pb	31.2	0.08	0.9986	0.70	3.0	0.48	0.9242
Ni	5.9	0.02	0.9590	0.90	0.7	0.34	0.8901
Cu	9.1	0.03	0.9977	0.90	0.9	0.39	0.9213
Cd	6.5	0.31	0.9931	0.40	1.1	0.34	0.8536
Co	5.8	0.01	0.4936	0.95	0.5	0.37	0.8096

The experimental values obtained for the maximum sorption capacity of the biomass shown in Table 3.4 is close to the calculated values derived from the isotherm parameters.

At pH 5.5 coconut shell, Kudzu bark, Oak and Aspen had adsorption capacity of 2.6, 8.2, 0.5, and 0.9 mg copper/g respectively (Demirbas, 2008); 3.5mg Pb/g Okra waste (Hashem, 2007); an adsorption capacity of 8.6mg/g was recorded when rice husk was used to remove cadmium from solution (Kumar and Bandyopadhyay, 2006); likewise Annadurai et al. (2003) reported sorption capacities of 3.3mgPb/g, 2.9mgNi/g, 1.8mgCu/g and 1.2mgCo/g onto water treated banana peel. The result obtained in this study, with the unmodified plant tissues, showed that the capacity of *Delonix regia* pods compares well with most of the unmodified low-cost sorbent materials. *Delonix regia* would be a good sorbent to be used in the developing nations and also it could be very good to use for other countries of the world if the material is chemically modified or converted to biochar or activated carbon.

Table 3-4: Experimental and Calculated adsorption capacities of *Delonix regia* pods for Pb, Ni, Cu, Cd and Co

Metal ions	$Q_{e\ cal}$ (mg/g)	$Q_{e\ exp.}$ (mg/g)
Pb	31.2	30.3
Ni	5.9	6.0
Cu	9.1	8.9
Cd	6.5	6.4
Co	5.8	6.8

3.3.4 *Recovery or desorption of metals*

The recovery or desorption experiment was done to determine the reusability of the biomass and possible recovery of the metals. The result obtained is shown in Figure 3.7.

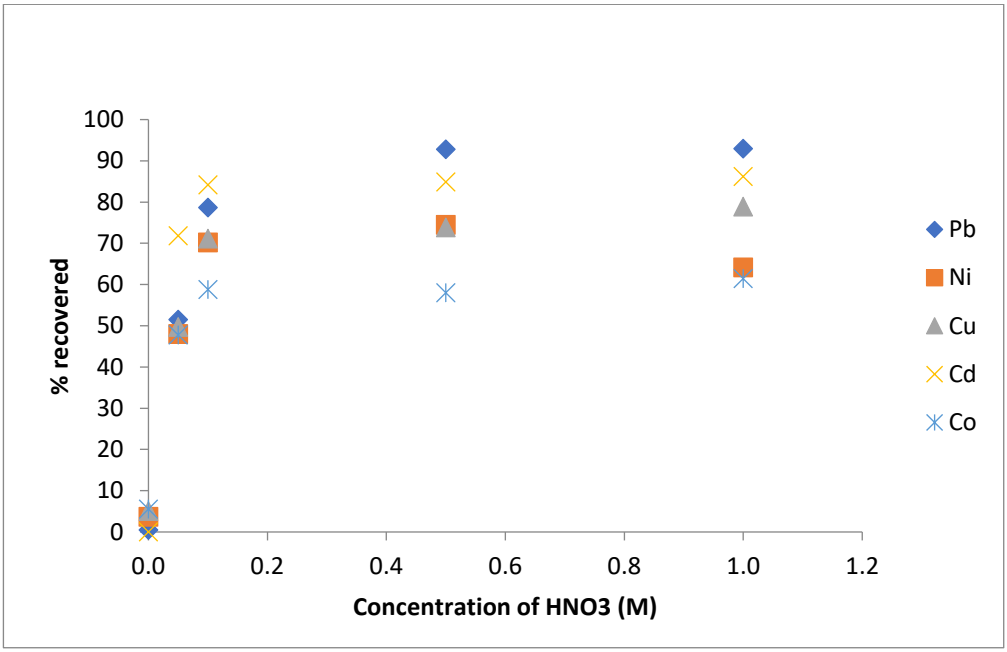


Figure 3-7: Recovery Study of Pb, Ni, Cu, Cd and Co adsorbed on *Delonix regia* pods {pH: 4-6; contact time: 30mins; metal ions concentration: 100ppm; adsorbate volume:20mls; biosorbent dose: 0.5mg, shaking rate:18rpm; temp:21^{o}C ±2}

The result of the experiment presented in Figure 3.7 showed that relatively low concentration of nitric acid (0.1M HNO_3) could be used to recover more than 50% of all the adsorbed metals from the biomass. With higher concentration of nitric acid, recovery of the metal ions did improve significantly.

3.3.5 *The effect of ionic strength*

The ionic strength of a solution which is a measure of the total concentrations of electrolytes in the solution is a main characteristic of solutions with dissolved ions; it

affects important properties of the solution. The effect of ionic strength can be observed from Figure 3.8.

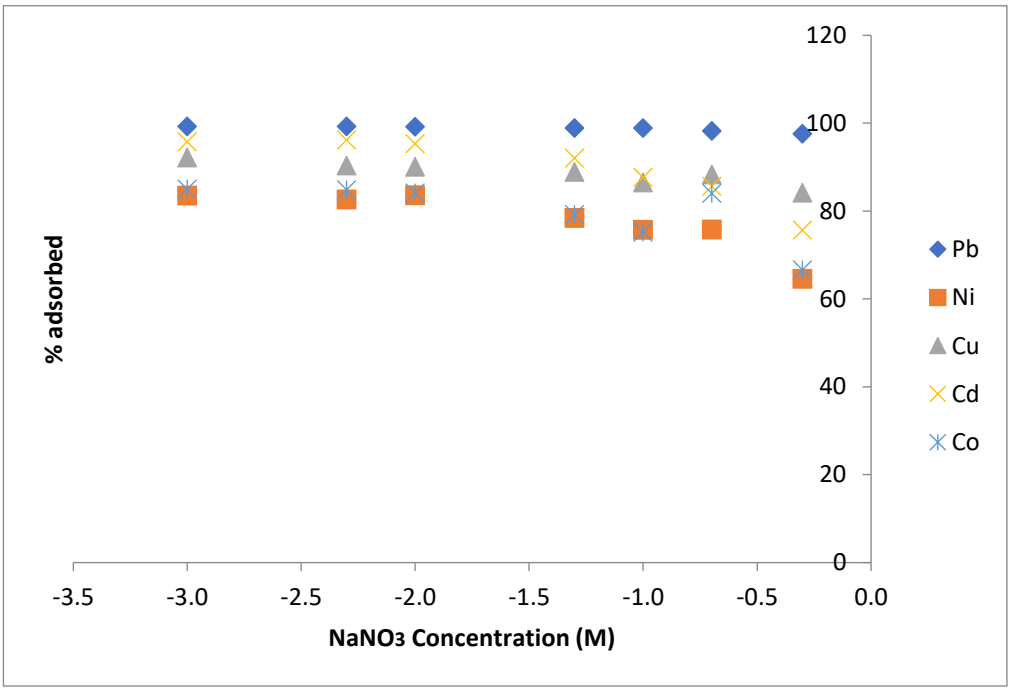


Figure 3-8: The effect of ionic strength on the adsorption of Pb, Ni, Cu, Cd and Co by *Delonix regia* pods{pH:4-6; contact time: 30 mins.; adsorbate concentration: 100ppm; adsorbate volume: 20mls; biosorbent dose: 5mg; shaking rate: 18rpm; temp.: 21±2^{o}C.

The uptake of the metal ions was reduced with increasing concentration of sodium ions. As the ionic strength of the solution increased, there was a decrease in the activity of the aqueous solutions which will consequently result in a decrease in metal uptake by *Delonix regia*. Increase in ionic strength leads to apparent decrease in the dissociation constant which result in a decrease in observed capacity. The presence of multivalent ions (especially in the salts from which the metals solution used in this experiment were prepared) in solution are able to contribute strongly to the ionic strength of the solutions and thus a reduction in adsorption capacity of *Delonix regia* for the metals. The ionic strength of the solutions containing a mixture of the electrolyte and the different targeted metal ions in this study are in the following

order: Ni>Co>Cd=Cu=Pb. At the highest level of solutions' ionic strength considered in this experiment, *Delonix regia* pods had above 65% adsorption for each of the metals thus its sorption ability in solutions of high ionic strength was not badly affected.

The difference in the effect of ionic strength on the metals could be attributed to the properties of ions (cations and anions) of the metal salts. A corresponding decrease in metal ions uptake with increasing ionic strength can also be attributed to decreasing activity of metal ions in solution.

3.3.6 *Effect of Adsorbent Doses*

This experiment was conducted to observe the effect of varying the quantity of adsorbent contacted with metal solutions while other experimental conditions remained the same on the sorption ability of *Delonix regia* pods. Result of the experiment to determine the effect of *Delonix regia* dosage on the sorption shown in Figure 3.9.

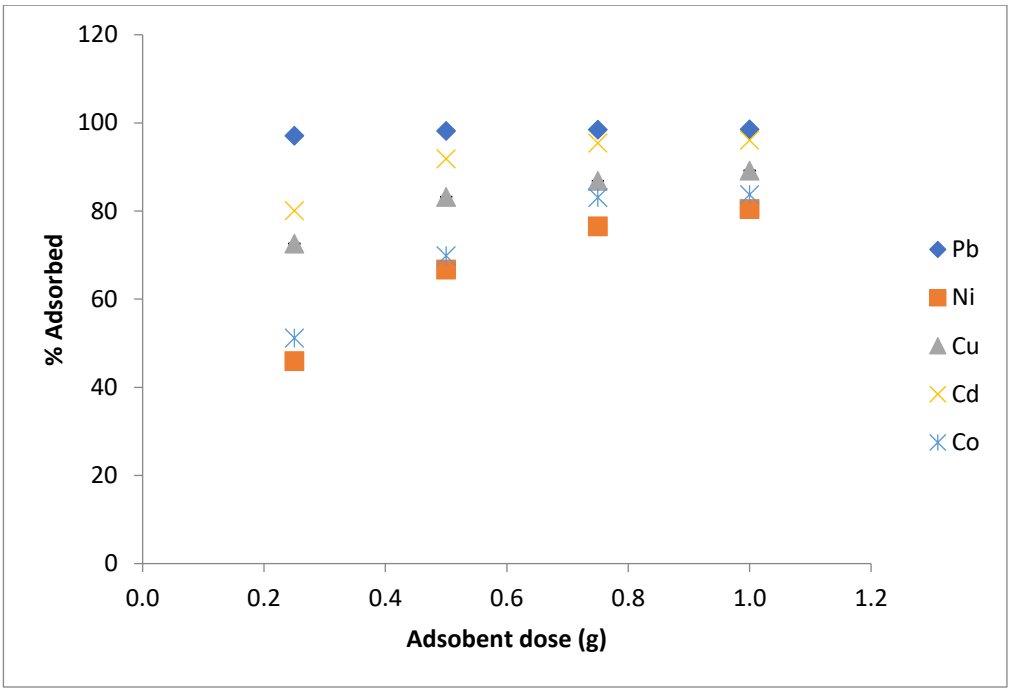


Figure 3-9: The effect of Adsorbent dose on the adsorption of Pb,Ni,Cu,Cd and Co by *Delonix regia* pods{pH:4-6; contact time: 30 mins.; adsorbate concentration: 100ppm; adsorbate volume: 20mls; biosorbent dose: 0.25g-1.0g; shaking rate: 18rpm; temp.: 21±2^{o}C

It revealed that there was gradual increase in amount of each metals adsorbed, except for Pb, with increasing doses of the adsorbent. This observation can be attributed to the increase of the adsorption surface area and the availability of free adsorption sites as dose increases. The only exception to this observed trend is lead whose uptake seemed not to be affected by the dose of adsorbent used. This might possibly be due to agglomeration of the biomass particles together when larger amounts are present in lead solution, thus reducing the available sites exposed for lead sorption.

3.4 Conclusion

The surface functional groups of the biomass and the solubility of ions in aqueous solutions is highly dependent on the pH of the solutions. The optimum experimental

pH for the sorption of lead, nickel, copper, cadmium and cobalt onto *Delonix regia* pods powder are 4, 5, 4, 6 and 4 respectively. This indicated that the adsorption experiment is pH-dependent and that maximum sorption of each of these metals onto *Delonix regia* is achievable at these corresponding values.

Very fast uptake of the metals by *D.regia* was observed within the first fifteen minutes of interaction, this is desirable for industrial operation. For this work, a contact time of thirty minutes was used for all the metals of interest. Kinetic models for lead, nickel, copper, cadmium and cobalt gave a linear relationship when t/Q_t was plotted against t; this means that second order kinetic which may involve forces through sharing or exchange of electrons is applicable. The high R^2 of the plots is also a confirmation of the applicability of this model. Low values of the rate constant showed that the process achieves equilibration quickly and in this order Pb>Cd>Co>Cu>Ni.

The effect of initial metal concentration on adsorption by *D.regia* pods showed that metal uptake increased with increasing initial metal concentrations. It means the sorption is dependent on the initial metal concentration. *Delonix regia* will be effective in the removal of lead when the solution concentration less than 500 ppm; nickel, copper and cadmium less than 400 ppm and for cobalt it will be effective up to 100 ppm. Sorption isotherms expressing the relation between the amount of adsorbent and the metal ion concentration in solution at equilibrium showed that the Langmuir and the Freundlich Isotherms were applicable for these the sorption processes. Depending on the initial metal ion concentration, Langmuir isotherm was found to be suitable when concentration is below 200 ppm with the exception of cobalt, in which case it was favourable below 100 ppm while Freundlich Isotherm is better over a wider concentration range. The efficiency of the adsorption process follows the order:

Pb>Cu>Co>Cd=Ni with the maximum capacity of *Delonix regia* pod powder being 31.2mgPb/g; 5.9mgNi/g; 9.1mgCu/g; 6.5mgCd/g and 5.8mgCo/g.

Studies on ionic strength revealed that the higher the solutions' ionic strength, the lower the recorded uptake by *D.regia* pods; increasing the dose of *D.regia* resulted in increased percentage adsorbed except for lead where the dose has no effect on the percentage of metal adsorbed.

Recovery study showed that low concentration of nitric acid could be used to recover some amount of adsorbed metal but increasing the concentration of the acid resulted in a recovery of above 70% of each of the metals, thus recovery of the metal ions adsorbed on the biomass could be effectively achieved by using moderately high concentration of nitric acid.

Chapter 4. Investigating the Adsorptive Capacity of *Delonix regia* Leaves for the Removal of Heavy Metals from Waste Water

4.1 Introduction

The global environment is polluted and adversely affected through activities such as mining operations, industrialization and urbanization which have accelerated the fluxes of heavy metals in the ecosystem via wastewater disposal. The need for economical and safe methods for the removal of heavy metals from waters has aroused research interest into the investigation of low cost alternatives to the commercially available activated carbon. As a result of this, there is need to explore all possible agro-based inexpensive adsorbents and study their feasibility for heavy metal removal in wastewater (Renge and Khedkar, 2012).

Natural materials are considered one of the sources for low cost sorbent, but for a natural material to be suitable as a low-cost sorbent it must be locally and easily available in large quantities; should not be expensive and be of little or no economic value (Mohan and Pittman, 2007).

The above definition described the leaves of the *Delonix regia* tree very well as it is the most abundant part of the tree that also require little or no processing before it can be used for investigation. Other parts of the tree such as the bark or the seeds could also be explored but for some contingencies involved during processing; for instance, if the bark is used for investigation and found to be very efficient, that will result in the death of the tree itself because so many trees have to be exposed as they are stiped off their barks before enough quantity could be obtained. As for the seeds, they are enclosed in very tough skin coat that require great efforts to split open or possibly applying great heat to turn the seed coat into carbonaceous material before it can be

used. Thus, as far as the definition for low cost adsorbent is concerned, the leave of the tree is the best choice to consider. There has been no reported research on the leaves of the *Delonix regia* except in Orthodox medicine where it was reported to have glucose lowering capacity (Modi et al., 2016, Rahman et al., 2011).

Research had been done on the use of tree leaves but the major focus is on organic with very few reports on the use of plants leaves as adsorbents for inorganic pollutants. SHARMA and Imran (2011) reported that Mango leave powder was used for the removal of Rhodamine B dye and removal efficiency of 77% was recorded in 45 mins contact time.

Dried pandanus leaves were used as activated carbon to remove Congo red, Malachite green and Rhodamine B dyes from solutions. The result showed that over 60% of each type of dye could be removed by Pandanus leaves depending on the operating temperature (Hema and Arivoli, 2007). Acid carbonized Phoenix Sylvestric leaves was reported by Arivoli and Henkuzhali (2008) to remove about 90% of Rhodamine B from solution at 60^{o}C.

Saha and Saha (2014) reported the efficiency of using mango leaves for the removal of Cr (VI) from solution while the use of Mango bark and Neem bark for the removal of mercury (II), chromium (III) and cadmium (II) was reported by Tiwari et al. (1999). Commercially available tea leaves were reported to have adsorption capacities of 0.4, 0.3 and 0.2 mmol/g for Pb, Cd and Zn respectively (Tee and Khan, 1988).

My work in this chapter continues the investigation of agricultural waste with focus on the less fibrous part by studying/ investigating the adsorption capacities of powder made from *Delonix regia* leaves for the sorption of lead, nickel, copper, cadmium and cobalt from aqueous solutions. It will also include:

(a) the determination of some basic parameters such as the pH, ionic strength, contact time and initial concentration of heavy metal at which *Delonix regia* leaves could be used efficiently for the removal of heavy metals from polluted water;

(b) determining the kinetic and Isotherm constants of the adsorption process;

(c) investigate recovery capabilities of the bound metals from the spent biomass using various concentrations of nitric acid.

4.2 Methods

The experimental procedure used in this chapter of the work is in Section 3.2. The difference is that for this chapter dried and grounded leaves of *Delonix regia* was used as the adsorbent.

4.3 Results and Discussion

4.3.1 *The effect of pH on Adsorption*

In adsorption processes the pH of a solution also referred to as its hydrogen ion concentration, is considered as one of the most important parameters that influence the adsorption behaviour of metal ions in aqueous solutions. It affects the solubility of the metal ions in solution, replaces some of the positive ions found in the active sites and affects the degree of ionization of the adsorbate during the reaction (Pehlivan et al., 2012, Saifuddin and Kumaran, 2005). The plot in Figure 4.1 is the result obtained from the effect of pH on the adsorption process using *Delonix regia* leaves.

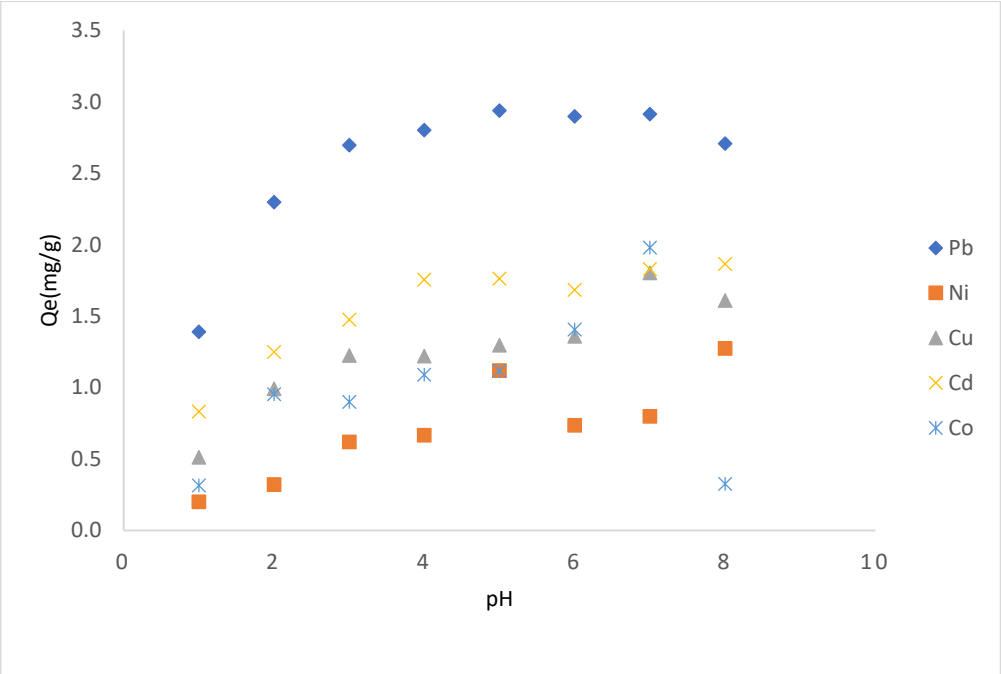


Figure 4-1: The effect of pH on the adsorption of Pb, Ni, Cu, Cd and Co by *Delonix regia* leaves{pH: 1-8; contact time: 300 mins; metal ions concentration:100ppm; adsorbate volume:20mls; biosorbent dose: 0.5g, shaking rate:18rpm; temp:21^{o}C ±2}

From this it is seen that the uptake of lead increased steadily to pH 3 after which it fairly constant to pH 7 where 2.9 mg/g uptake was achieved. pH 5, the point at which the maximum observed uptake of 2.9 was recorded was used as the experimental pH for other experiments. pH 5.0 was reported by Pehlivan et al. (2012) as the uptake pH for lead using sugar beet pulp and some other reports also have similar results for sorption of lead on bulrush biomass (*Schoenoplectus californicus*) (Bueno et al., 2008, Saeed et al., 2002).

Nickel had a maximum adsorption of 1.1 mg/g at pH 5, before attaining this value its uptake values had increased from 0.2 to 0.7 mg/g at pH 4. Decrease in uptake were observed at pH 6 and 7 respectively. In 2005, Saeed *et al.* reported optimum nickel sorption at pH 6 for its sorption on crop milling waste (black gram husk) (Saeed et al.,

2005), while a pH of 5 was reported for natural neem sawdust and almond husk (Hasar, 2003, Rao et al., 2007).

The uptake value obtained for the sorption of copper gradually increased throughout the experimental pH values considered. Though increases were recorded at pH 6 and 7 but visible precipitate had already been formed in the experimental set up at these pH values. Thus pH 5 was taken as the pH for other studies. Some studies reported optimum pH values of 5.0 and 5.8 for the uptake of copper from solutions using modified jute fibres; a composite from egg shell and chitosan (Anantha and Kota, 2016, Shukla and Pai, 2005, Witek-Krowiak et al., 2011).

A series of uptake values from 0.8 mg/g, to 1.8 mg/g were obtained for cadmium within the experimental pH values of 1 to 7 considered in this work. pH 5 was set as the working pH. Cadmium was reported to have a maximum uptake at pH 5 on crop milling waste and sugar beet pulp (Pehlivan et al., 2012, Saeed et al., 2005) and pH 6 on mushrooms (Vimala and Das, 2009).

The uptake recorded for cobalt at various investigated pH increased from pH 1 through 7. For the purpose of this study, pH 5 was chosen as the working pH for subsequent experiments with cobalt. Cobalt was reported to have a maximum uptake at pH 5 for its sorption on *Amaranthus hydridus* wastes (Egila et al., 2010) and pH 8 unto activated bentonite (Al-Shahrani, 2014).

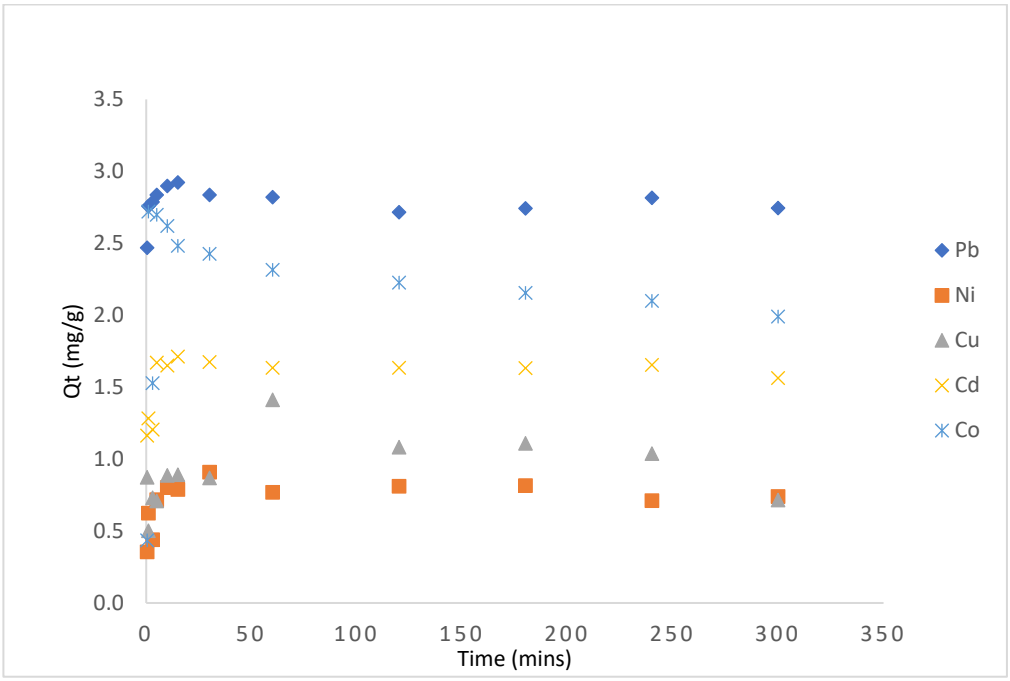
In the low pH values (1-3) adsorption sites are more protonated and they are less attractive against various cationic forms of metals i.e. electrostatic repulsion will be high. Electrostatic repulsion decreases with increasing pH due to a reduction of positive charge density on the sorption edges thus resulting in an increase in metal biosorption (Ajmal et al., 2000, Sari et al., 2009). At pH values higher than 7, the

quantity of metallic ions taken up was decreased due to the formation of soluble complexes of the metal ions and their competition with the active sites. Moderate adsorption for Pb, Cu and Cd even at low pH is an indication that the *Delonix regia* leaves could be useful in the treatment of mine acid drainage and tailings and some related industries as the pH of the wastes generated from these sectors is in the low pH range.

4.3.2 *The Effect of Interaction time on Adsorption by Delonix regia leaves*

The investigation of the interaction time shown in Figure 4.2 is an important aspect to consider when designing an industrial reactor because of the economy of operation and for gaining insights into the kinetics involved during the sorption process.

(a)



(b)

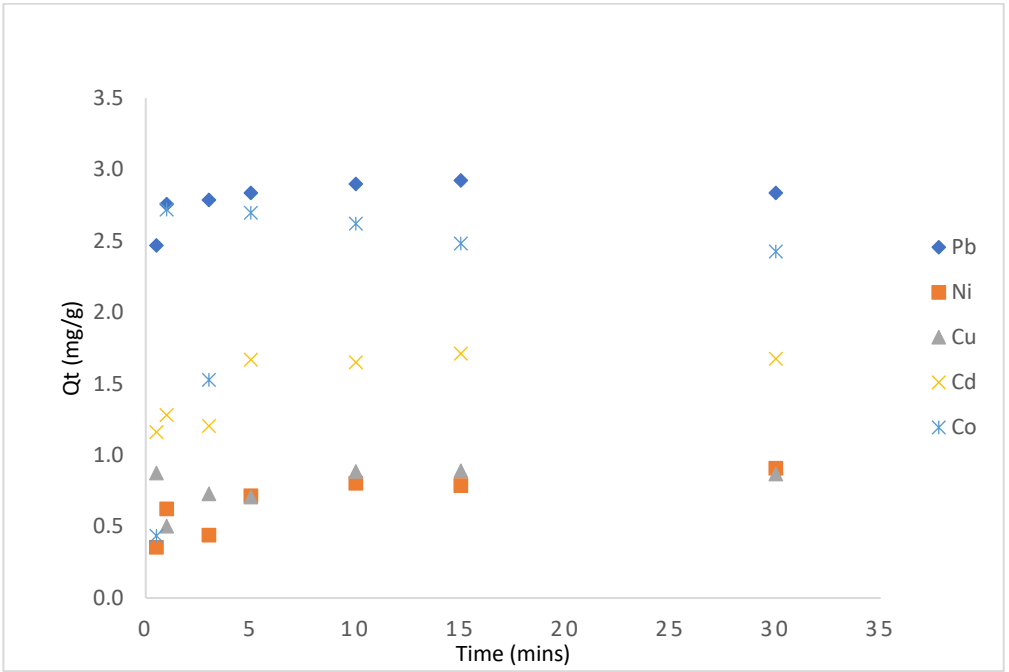


Figure 4-2: The effect of interaction time on the adsorption of Pb, Ni, Cu, Cd and Co by *Delonix regia* leaves {pH: 5; contact time: 1- 300 mins.; adsorbate concentration: 100ppm; adsorbate volume: 20mls; biosorbent dose: 5mg; shaking rate: 18rpm; temp.: 21±2ºC

The study began with a 1-minute contact time for all the metals considered, at which the uptake recoded for lead, nickel, copper, cadmium and cobalt were 2.7 mg/g, 0.6, 0.5, 1.3 and 2.7 mg/g respectively.

The uptake for lead increased from the start of the study and above 90% adsorption was recorded at 30 minutes contact time before a continuous decrease was observed over the remaining time frame of the experiment. The uptake of nickel by the leaves of *Delonix regia* throughout the experimental contact time was between 16 to 23% sorption.

After the initial value of 0.5 mg/g at 1-minute contact with the *Delonix regia* leaves powder, the uptake of copper by the adsorbent increased gradually to 51% at 60 minutes contact time between the adsorbent and copper solution after which sharp decrease were recorded.

Cadmium and cobalt have a percentage uptake of 69% and 51% respectively at 30 minutes of contact with the adsorbent. The uptake rate for all the investigated metals was rapid within the first 15 minutes of contact, after which it began to decrease. This is probably due to larger surface area of the leaves being available at the beginning for the adsorption of metal ions. Though an experimental time of 30 minutes was chosen in this study for easy set-up, the actual equilibrium time was 15 minutes. The results obtained in this study are close to the reports in a study on activated carbon from cow waste by (Elaigwu et al. (2009) where equilibrium time of 80 minutes for lead and 60 minutes for cadmium respectively were reported.

4.3.2.1 Kinetic modelling in a batch system

The study of reaction kinetics gives an insight into the reaction mechanisms i.e. the sequence of bond making and bond breaking steps in chemical reactions. When the biomass is employed as a free suspension in a well-agitated batch system, all binding sites are made readily available for metal uptake so the effect of external film diffusion on sorption rate can be assumed not significant and ignored in any engineering analysis (McKay et al., 1999), thus external film diffusion is not considered as a necessary mechanism in an agitated system. In order to investigate the mechanism of sorption and potential rate controlling steps such as mass transport and chemical reaction processes, kinetic models have been used to test experimental data obtained from interaction time experiments. Experimental data obtained from an interaction time study was found to obey the pseudo-second order kinetic model and thus was reported in this work in Figure 4.3.

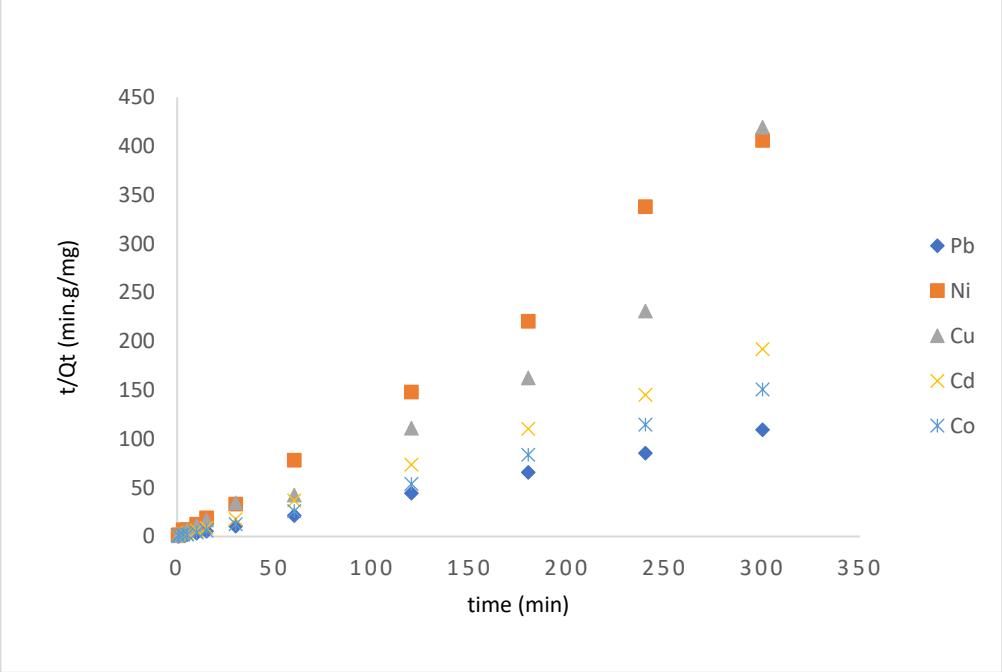


Figure 4-3: Pseudo- second order kinetics study of the adsorption of Pb, Ni, Cu, Cd and Co by *Delonix regia* leaves {pH: 5; contact time: 1-300 mins.; adsorbate concentration: 100ppm; adsorbate volume: 20mls; biosorbent dose: 5mg; shaking rate: 18rpm; temp.: 21±2^{o}C.

The pseudo-second-order equation is based on the sorption capacity of the solid phase, pseudo-second order model predicts the behaviour over the whole range of adsorption and is in agreement with an adsorption mechanism being the rate controlling step. If the rate of sorption is a second-order mechanism, the pseudo second-order chemisorption kinetic rate equations are expressed in equations 4.1 to 4.4:

$$\frac{dQ_t}{dt} = k_{2,ad}\left(Q_{eq} - Q_t\right)^2 \text{.....Equation 4-1}$$

where $k_{2,ad}$ is the rate constant of second-order adsorption (g mg^{-1} min^{-1}). For the boundary conditions t=0 to t=t and Q_t=0 to Q_t=Q_e; the integrated form of the equation becomes

$$\frac{1}{(Q_{eq}-Q_t)} = \frac{1}{Q_{eq}} + k_{2,ad} \text{.....Equation 4-2}$$

which is the integrated rate law for a second-order reaction. This equation can be rearranged to obtain

$$Q_t = \frac{t}{\frac{1}{(k_{2ad}Q_{eq}^2)}} + \frac{t}{Q_{eq}} \text{..... Equation 4-3}$$

which has a linear form

$$\frac{t}{Q_t} = \frac{1}{k_{2,ad}Q_{eq}^2} + \frac{1}{Q_{eq}t} \text{..... Equation 4-4}$$

If second-order kinetics are applicable, the plot of t/Q_t against t should give a linear relationship, from which Q_{eq} and $k_{2,ad}$ can be determined from the slope and intercept of the plot (Ho and McKay, 1999b, Ho and McKay, 1999c, Ho and McKay, 1999a, McKay et al., 1999). From Figure 4.3, a straight line shows the applicability of this

model. Table 4.1 show the correlation factor R^2, second order rate constant $k_{2,ad}$ and adsorption capacity Q_e for each metal.

Table 4-1: Adsorption parameters obtained from the second order kinetics model for the sorption of metals unto *D.regia* leaves.

Metals	**Q_{eq} (mg/g)**	**$k_{2,ad}$ (g/mg/min)**	**R^2**
Lead	2.8	-7.5	0.9997
Nickel	0.7	-0.25	0.9958
Copper	0.8	-0.09	0.9373
Cadmium	1.6	-1.28	0.9988
Cobalt	2.6	-0.22	0.9692

4.3.3 *Effect of initial metal concentration on adsorption*

The initial concentration of the metal in solution is an essential force that is required to overcome mass transfer resistance of the metals between the aqueous and solid phases. The result shown in Figure 4.4 is from the experiment of using different concentrations of adsorbate with fixed mass of adsorbent.

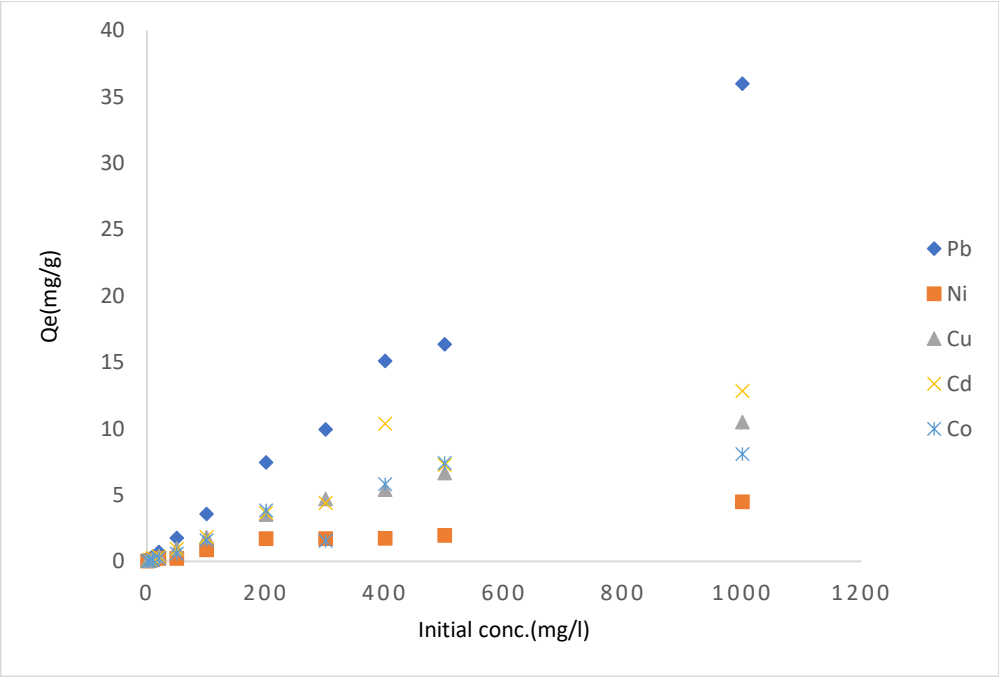


Figure 4-4: The effect of initial concentration on the adsorption of Pb, Ni ,Cu, Cd and Co by *Delonix regia* leaves {pH: 5; contact time: 30 mins.; adsorbate concentration: 1-1000ppm; adsorbate volume: 20mls; biosorbent dose: 5mg; shaking rate: 18rpm; temp.: 21±2^{o}C.

This result showed that the uptake of each of the metals by *Delonix regia* leaves was increasing with increase in adsorbate concentration.

Higher concentration of metals result in an increased concentration gradient which probably result in higher degree of interaction between the metals and the sorption sites of the adsorbent, resulting in a higher uptake of the metals (Zhang and Wang, 2015). Although there was increase in uptake with increase in initial metal concentration, the increase in percentage sorption was gradually reduced showing that the sorption sites on the adsorbent were saturated.

4.3.3.1 Equilibrium Modelling for batch adsorption system

Equilibrium data, commonly known as the equilibrium sorption isotherm is fundamentally important in the design of sorption systems and provide information on

the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions (Aksu and İşoğlu, 2005). It is described by sorption isotherm characterized by certain constants whose values express the surface properties and affinity of the sorbent. Also, equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually as the ratio between the quantity sorbed and that remaining in solution at fixed temperature at equilibrium (El-Bayaa et al., 2009). The Langmuir and Freundlich equations are in common use for describing adsorption isotherms at a constant temperature for water and wastewater treatment applications.

In order to determine the isotherm parameters for the adsorption of the investigated metals onto *Delonix regia* leaves powder, data obtained from the effect of concentration shown in Figure 4.4 where various concentrations (1, 5,10, 20, 50, 100, 200, 500 and 1000ppm) of the metal solutions were contacted with the adsorbent, was used for the isotherm modelling. The data obtained fitted well to the Freundlich Isotherm as shown in Figure 4.5 and Table 4.2.

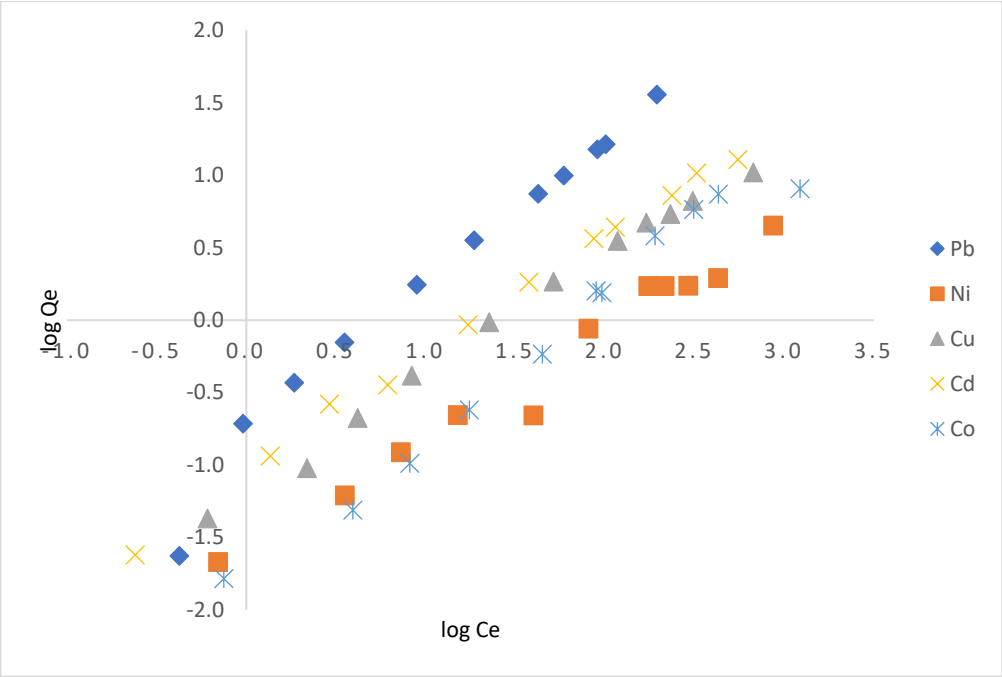


Figure 4-5: Plot of Freundlich Isotherm for the adsorption of Pb, Ni, Cu, Cd and Co by *Delonix regia* leaves{pH: 5; contact time: 30 mins.; adsorbate concentration: 1-1000ppm; adsorbate volume: 20mls; biosorbent dose: 5mg; shaking rate: 18rpm; temp.: 21±2°C.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems (Özcan and Özcan, 2004). The Freundlich equation is expressed in equations 4.5 and 4.6:

$Q_{e} = K_F C e^{1/n}$ (non- linear form) …… Equation 4-5

$Log\ Q_e = Log\ K_F + \frac{1}{n} Log\ C_e$ (linear form) …… Equation 4-6

where K_F and n are Freundlich constants with K_F (mg/g (L/mg)$^{1/}n$) the adsorption capacity of the sorbent and n giving an indication of how favourable the adsorption process is. The magnitude of the exponent, 1/n, gives an indication of the favourability of adsorption. Values of $n > 1$ represent favourable adsorption condition (Ho and McKay, 1998, Poots et al., 1978). To determine the constants K_F and n, the linear form of the equation (equation 4.6) may be used to produce a graph of Log(Q_e)

against Log(C_e) (shown in Figure 4.5) from which the values of K_F and n are calculated from the intercept and slope of the plot.

Table 4-2: Adsorption parameters for Freundlich Isotherm describing the sorption of Pb, Ni, Cu, Cd and Co unto *Delonix regia* leaves

Metals	**K_F**	**n**	**R^2**
Lead	0.14	0.9251	0.976
Nickel	0.03	1.3326	0.9748
Copper	0.07	1.2299	0.9937
Cadmium	0.06	1.2370	0.9966
Cobalt	0.02	0.9980	0.9847

4.3.4 *Adsorption capacity study*

The experimental adsorption capacity for *Delonix regia* leaves are 10.3 mg Pb/g; 10.3 mg Ni/g; for copper it was 9.2 mg/g; 8.4 mg Cd/g and 10.3 mg Co/g.

The adsorption capacity of *Delonix regia* leaves was investigated by carrying out seven cycles in this adsorption experiment. At the first cycle, 7.6mg/g of lead was taken up by the adsorbent, during the second cycle the uptake value increased to 10.3mg/g after which it decreased to the seventh cycle. The adsorption capacity study in the case of nickel began with an uptake of 1.7mg/g at the first cycle and increased to 10.3 at the second cycle, and after the second cycle a fluctuating pattern was observed for the rest of the cycles. The uptake for copper in the second cycle was 9.2 mg/g, a value equivalent to 72% sorption and just like the cycles for lead metals it decreased at the third cycle. Recorded uptake values were 4.7 and 8.4 mg/g cadmium

in the first and second cycles, decrease in uptake was recorded from the third cycle to the end while for cobalt, an uptake of 2.2, 9.4 and 10.3 mg/g were obtained in the first, second and third cycles respectively with a reduction to 6.3 at the fourth cycle.

Similar work carried out using different low cost adsorbents such as Sugar cane bagasse, Flax, Spruce were reported to have a capacity of 0.3 mg/g, 5.5 and 1.3 mg/g respectively for the sorption of copper at pH 5.5 (Demirbas, 2008); using Corncobs for the removal of lead from solution had a capacity of 8.3 mg Pb/g while Rubber leaves powder had a capacity of 47.7 mg/g for the sorption of lead (Ibrahim et al., 2010); Jute fibre had 3.37 mg/g capacity for the sorption of nickel (Shukla and Pai, 2005); water treated orange peels have sorption capacities of 2.3 mg Pb/g, 1.7 mg Ni/g, 1.4 mg Cu/g and 1.0 mg Co/g (Annadurai et al., 2003). *Delonix regia* leaves performed better than some of the unmodified agricultural wastes in the sorption the targeted heavy metals and could thus be used for removing them from waste water.

Delonix regia leaves being an agricultural material that is widely available in the tropical parts of the world and is considered as a waste because it has no economic value, will be a viable option especially for Nigeria where wastewater treatment is neglected because of associated cost.

4.3.5 *Effect of Ionic Strength*

The effect of the presence of electrolytes on the uptake of the metals was investigated using different concentrations of sodium ions. The result shown in Fig. 4.6 revealed that the presence of sodium ions reduced the uptake of lead, nickel, copper, cadmium and cobalt.

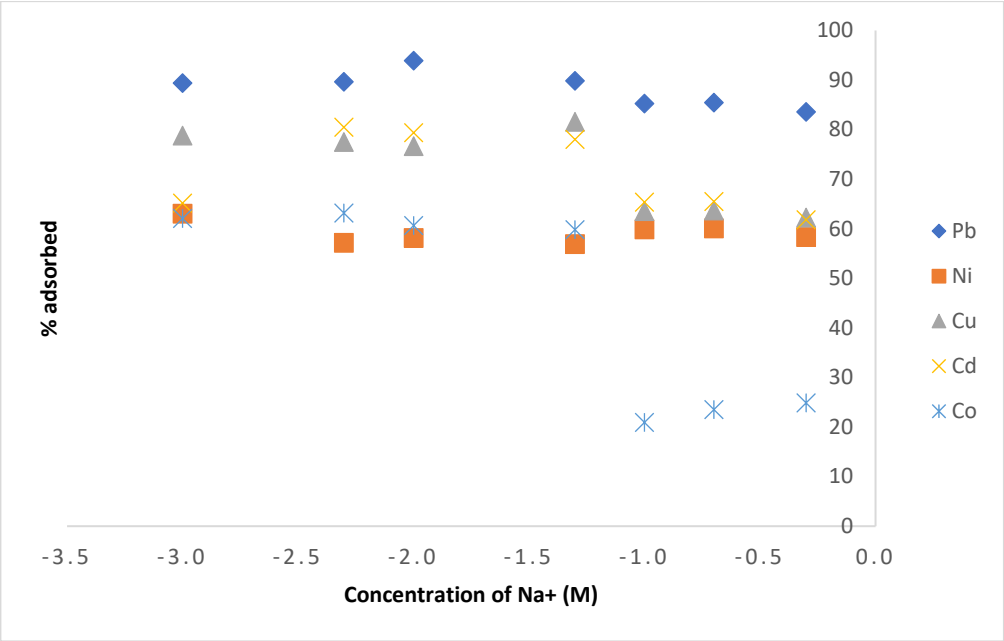


Figure 4-6: The effect of ionic strength on the adsorption of Pb, Ni, Cu, Cd and Co by *Delonix regia* leaves {pH: 5; contact time: 30 mins.; adsorbate concentration: 100ppm; adsorbate volume: 20mls; biosorbent dose: 5mg; shaking rate: 18rpm; temp.: 21±2^{o}C

Generally, decrease in uptake with increasing concentration of the electrolytes was observed for all investigated metals. The plots showed that the uptake values decreased with increase in ionic strength of the salt solutions for the five metal ions under study. The ionic strength of a solution which is a measure of the total concentrations of electrolytes in the solution is a main characteristic of solutions with dissolved ions; it affects important properties of the solution. Increase in ionic strength leads to apparent decrease in dissociation constant which result in a decrease in observed capacity. The presence of multivalent ions in solution strongly increase the ionic strength of the solution and thus leads to a reduction in capacity. The ionic strength of the solution containing a mixture of the electrolyte and the different metal ions are different following the order: Ni>Co>Cd=Cu=Pb. The difference in the effect

of ionic strength on the metals could be attributed to the properties of ions (cations and anions) of the metal salts.

A corresponding decrease in metal ions uptake with increasing ionic strength can also be attributed to decreasing activity of metal ions in solution.

4.3.6 *Effect of Biosorbent Dose*

Result of the experiment to determine the effect of the adsorbent dose on the sorption is shown in Figure 4.7. This experiment was conducted to investigate what happens to sorption capacity of *Delonix regia* pods by changing the amount of the adsorbent used in the experiment while other factors were kept constant.

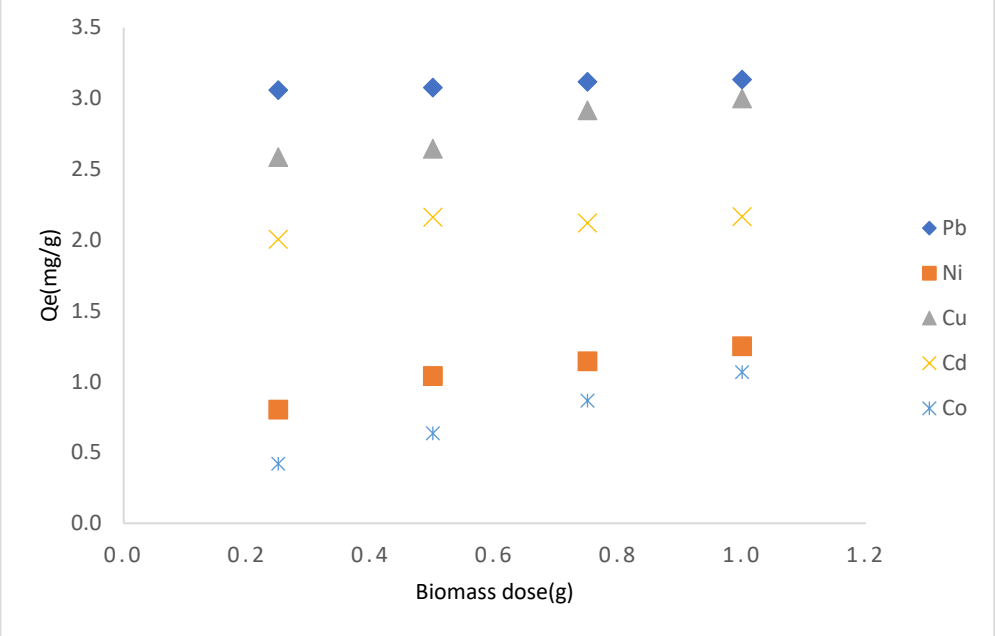


Figure 4-7: The effect of biosorbent dose on the adsorption of Pb, Ni, Cu, Cd and Co by *Delonix regia* leaves {pH: 5; contact time: 30 mins.; adsorbate concentration: 100ppm; adsorbate volume: 20mls; biosorbent dose: 0.25- 1.0mg; shaking rate: 18rpm; temp.: 21±2^{o}C.

It revealed that there was gradual increase in amount of lead, nickel, copper, cadmium and cobalt adsorbed with increasing mass of grounded *Delonix regia* leaves from 0.25, 0.5, 0.75 and 1.0g. This observation can be attributed to be as a result of the increase in available adsorption site with increase in biosorbent dose. The effect of adsorbent dose on the uptake of lead and cadmium was similar as there was small increase in the uptake throughout the entire range of the doses investigated. Copper exhibited a slight increase in uptake from 2.6 to 2.9 mg/g when the dose was increased from 0.5 to 0.75g. The trend observed in nickel and cobalt also looked similar in that they both showed an increase in uptake as should be expected when the dose was increased for all the dosages considered. The increase in uptake observed for the metals, lead, nickel, copper, cadmium and cobalt, with increasing adsorbent dose can be due to the availability of free adsorption sites for the metals uptake.

4.3.7 *Recovery of metals*

The results of the metal recovery experiment are presented in Figure 4.8.

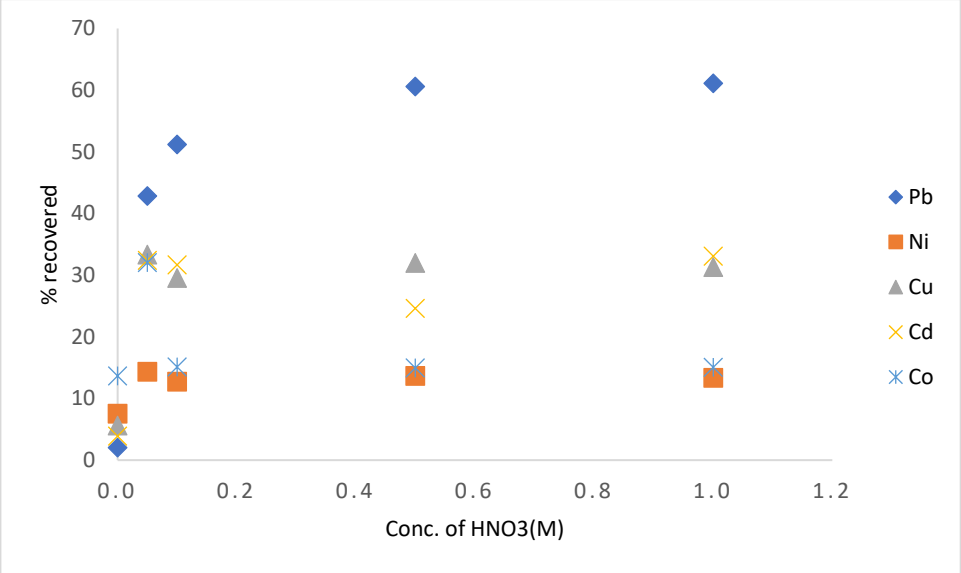


Figure 4-8: Recovery study of Pb, Ni, Cu, Cd and Co adsorbed on *Delonix regia* leaves {pH:5; contact time: 30 mins.; adsorbate concentration: 100ppm; adsorbate volume: 20mls; biosorbent dose: 5mg; shaking rate: 18rpm; temp.: 21±2^{o}C

The result showed that with 1.0 M HNO_3 less than 65% of the adsorbed metals on the adsorbent could be removed. A decrease was observed in the percentage of metals recovered with lower concentrations of the acid. Thus, the reusability of the adsorbent would not be economical since metal recovery from it might not really be a success at low acid concentrations.

4.3.8 *Comparison of the adsorption study on Delonix regia pods and leaves powder*

Comparison of the adsorption results obtained from the powder of *Delonix regai* pods and leaves showed that at pH 1 a certain degree between 16% to 27% sorption onto the pods was noticed for some metals (Pb, Ni and Cu); and at pH 2 and 3 the pod powder was effective to adsorb all studied metals; at pH 3 above 70% sorption was recorded except for nickel which has 52% uptake, whereas with the leaves, lower uptake was observed at these pH values for the studied metals; at pH 3, less than 60% uptake was observed except for lead that recorded 87% uptake at pH 3. At the optimum pH in this study, a decrease in maximum uptake by 4% Pb, 38% Ni, 34% Cu, 23% Cd and 48% Co was recorded in the leaves compared with the pods.

Fast metal uptake was observed in both materials, but the pod powder was able to adsorb efficiently within wider concentration ranges depending on the metal considered (500 ppm for lead, 400 ppm for nickel, copper and cadmium; and 100 ppm for cobalt). The leaves powder was effective only within a limited concentration range of less than 50ppm; outside this concentration the leave was no longer effective especially for lead and nickel sorption. The capacity results shown below suggest leave powder is better for the sorption of Ni, Cd and Co. The capacity obtained for the pods varied greatly from metals to metals **(30.3mgPb/g, 6.0mgNi/g, 8.9mgCu/g, 6.4mgCd/g, 6.9mgCo/g)** while in the leaves the capacity was confined to a certain

range of values **(10.3mgPb/g, 10.3mgNi/g, 9.2mgCu/g, 8.4mgCd/g, 10.3mgCo/g)**. *Delonix regia* pods powder is better for Pb; and both materials have the same capacity for Cu. Ionic strength effects on the sorption ability of both materials followed the same trend, but sorption of metals onto the pods showing better overall performance. The recovery experiment for all the studied metals however revealed that more than 60% of adsorbed metal ions on the pods can be recovered with low concentration of acid whereas the leaves was able to retain the adsorbed metals onto it as there was virtually no recovery of metals at low acid concentrations and less than 50% recovery was achieved with 1M nitric acid (highest concentration used for recovery in this work) expect in the case of lead.

4.4 Conclusion

pH which is defined as the concentration of hydrogen ions in solution is an important factor in adsorption as it affects the solubility of metal ions in solutions. The adsorption of lead, nickel, copper cadmium and cobalt onto *D.regia* leaves powder depends on the prevailing pH of the solution. Maximum lead, nickel, copper, cadmium and cobalt uptakes were observed at pH 5.

Metal uptake per time was seen to increase within the first thirty minutes of contact except for copper where increase in uptake was observed up to sixty minutes contact time. The noticed increased in copper uptake at sixty minutes is probably due to an error because the increase uptake at 60 minutes and the decrease afterwards were too significant as shown in Figure 4.2. Thus, thirty minutes experimental contact time was used for all the metals in this study. The kinetics of metal sorption unto *D.regia* leaves powder was best fitted to the second order rate equation having R^2 greater than 0.93

for each of the studied metals. The rate constants for each metal show the relative quickness of the process to approach equilibration with lead being in the first position; the order followed is Pb>Cd>Ni>Co>Cu.

Data obtained from concentration study fitted well with the Freundlich isotherm with R^2 greater than 0.97 for all studied metals. The favourability of the sorption was evaluated from the value a constant, n, which was calculated from the slope of the plot of Log Qe against Log Ce. The obtained n values showed the process to be favourable with experimental adsorption capacity of 10.3mgPb/g; 10.3mgNi/g; 9.2mgCu/g; 8.4mgCd/g and 10.3mgCo/g of *Delonix regia* leaves powder.

Generally, a decrease in metal uptake was observed when the ionic strength of solution was increased. Gradual increase in metal uptake was noticed as *D.regia* leaves dose was increased. The recovery study showed that less than 60% of adsorbed metals could be recovered by contacting the used *D.regia* leaves with high concentration of acid.

In conclusion, when the result obtained in the sorption study with the leaves were compared with that from the pods, the performance of the pods at different pH, wider concentration and different ionic strength conditions were better than those of the leaves and also the used pods powder have the possibility of reusage. The pods would be a better adsorbent for removing heavy metals from aqueous solution.

Chapter 5. Investigation of the potential of using *Delonix regia* pods and Biochar for remediating contaminated soils

5.1 Introduction

Contamination of soil by heavy metals have become an issue of global environmental concern in recent years (Zhang et al., 2013) due to waste emissions from industrial production, mining activities, wastewater irrigation and inadequate management of pesticides and chemicals in agricultural production. All these activities have led to increasingly more contaminated soils worldwide. Generally, metal pollutants in the soils are a threat to ecosystems, agricultural production, and human health. In 2012, (Petruzzelli) reported that soil contamination has been identified as an important issue for action in the European Community strategy for soil protection because it is estimated that 3.5 million sites in industrial and mine sites, landfills, energy production plants, and agricultural land in Europe are potentially contaminated. Pollutants (heavy metals) have to be in the soluble form before they can be available for uptake by plants. These soluble metal ions present in soil solution have different rate of exchange. Their availability to plants and soil dwelling organisms is controlled by physical, chemical and biological processes and interactions between them. The process of sorption of heavy metals in soil and their bioavailability is dependent on many soil properties such as: granulometric composition, organic matter content, occurrence and form of cations, pH value, sorption capacity, nutrients (macro and micro) (Fijałkowski et al., 2012) .

Soil remediation technologies are of special attention since conventional soil reclamation practices, i.e., landfilling and excavation, are often very expensive and environmentally unpractical, as compared to alternative options. Soil amendment

based technologies, such as soil immobilization/solidification, are cost effective and less environmentally disruptive (Kumpiene et al., 2008, Mulligan et al., 2001). Unlike organic pollutants which can be degraded, heavy metals impair their toxicity and mobility by triggering the important immobilization process, i.e., (ad)sorption, precipitation, complexation, and redox reactions, in the process of soil remediation (Adriano et al., 2004). In addition, biological and chemical stabilization of toxic heavy metals using organic (i.e., biosolids) and inorganic amendments (i.e., phosphate compounds and lime) are suitable options to minimize metal bioavailability (Park et al., 2011). In the urban environment, as more localized toxic heavy metals are found, the process of metal stabilization including chemical washing and phytoextraction have been applied for remediation. However, when phytoextraction is ineffective, alternate options, i.e., in-situ immobilization, are considered as an important part of environmental management. Both organic and inorganic soil amendments are components of remediation techniques applied to manage contaminated soils. Immobilization of toxic heavy metals can be achieved mainly through precipitation, complexation and adsorption, reactions which result in the redistribution of metals from solution phase to solid phase, thus reducing their transport and bioavailability in the soil (Bolan et al., 2003, Porter et al., 2004). A crucial point to consider in the immobilization of heavy metals, Pb, Cd, and Cu, in contaminated soils depends upon the local availability and financial implications of soil amendments.

Metals form both soluble and insoluble complexes with organic constituents in soil with the mechanisms involve specially depending on the type of the organic matter. The organic constituents in soil have a great affiliation to metal cations due to the existence of functional groups or ligands which can form chelates with metals. The alcoholic, phenolic, carbonyl, and carboxyl functional groups dissociate due to

increasing pH, thus enhancing ligand ion affinity towards metal cations (Mortensen, 1963).

Various methods, as discussed in Chapter two, have been used to remediate contaminated soils. Biochar can potentially be used to reduce the bioavailable and leachability of heavy metals in soils through adsorption and other physicochemical reactions. It has been proved by many studies that the application of biochar to soils lead to an observed decrease in metal uptake by plants because there is a reduction in the concentration of heavy metals in soil and /or water (Tang et al., 2013). Research was conducted by Karami et al. (2011) on regulating the mobility of Cu and Pb and their subsequent uptake by plants from the soil revealed that the addition of both biochar and compost reduced the levels of both metals in the shoot of ryegrass. A similar reduction in bioavailability of several heavy metals (Zn, Ni, Cd and Pb) was reported by (Méndez et al., 2012).

Biochar has been shown to behave as an efficient sorbent for various contaminants, either organic or inorganic, due to its large surface area and special structure (Tang et al., 2013). The work of Cao et al. (2015), where he produced biochar from dairy manure, reported that biochar has an appreciable capacity for Pb and atrazine sorption from aqueous solution, with removal as high as 100% for Pb while atrazine removal was 77%. The incorporation of biochar into soil was investigated by Jiang et al. (2012) and the report showed that the acid extractable Cu and Pb decreased by 19.7 - 100% and 18.8 – 77% respectively with the increase in dose of biochar amendment.

The aim of this chapter is to investigate the effectiveness of both *Delonix regia* and commercially available biochar for remediation of contaminated soils.

The chapter's objectives were set to reveal the effect of soil pH, organic matter, the initial metal concentrations and the aging on the remediation using biochar and *Delonix regia.*

5.2 Materials and Methods

5.2.1 *Materials*

Metal salts of copper chloride dihydrate, cadmium and lead nitrate were used to prepare the metal solution for contaminating the soils.

The s particulate form of Humic acid HA, was added to the soils in order to study the effect of organic matter on the removal efficiency of the metals by each of the treatment materials.

Sodium acetate, Ammonium acetate, and Methylated spirit were employed for the determination of the soils' CEC.

Calgon solution was used in the particle size analysis.

Calcium Chloride salt was used to prepare the solution for the exchangeable metal content in the soils.

Biochar from Bodfari Environmental, UK and *Delonix regia* pods were used for the remediation treatment.

Tropical soil from Nigeria was used as the soil samples for this work.

5.2.2 *Methods*

5.2.2.1 Soil sampling, amendments and treatments

Soil samples were collected from the field at a depth of 0-20cm from three different locations in Nigeria in October 2016.

The maps showing the geographical location of the collection sites are shown in Figures 5.1. Ekiti and Ijero soils were collected at location on Longitude 4.65 and Latitude 7.53. Ife soils were collected at locations on Longitude 4.57 and latitude 7.47. Ilesha soils were collected at points on longitude 5.07 and latitude 7.81. The sampling was done in transient (0m, 2m, 4m, 10m and 50m) at each of the locations and collected soils were air dried at room temperature, passed through a 2mm mesh sieve and stored in air tight plastic containers before being shipped to the United Kingdom.

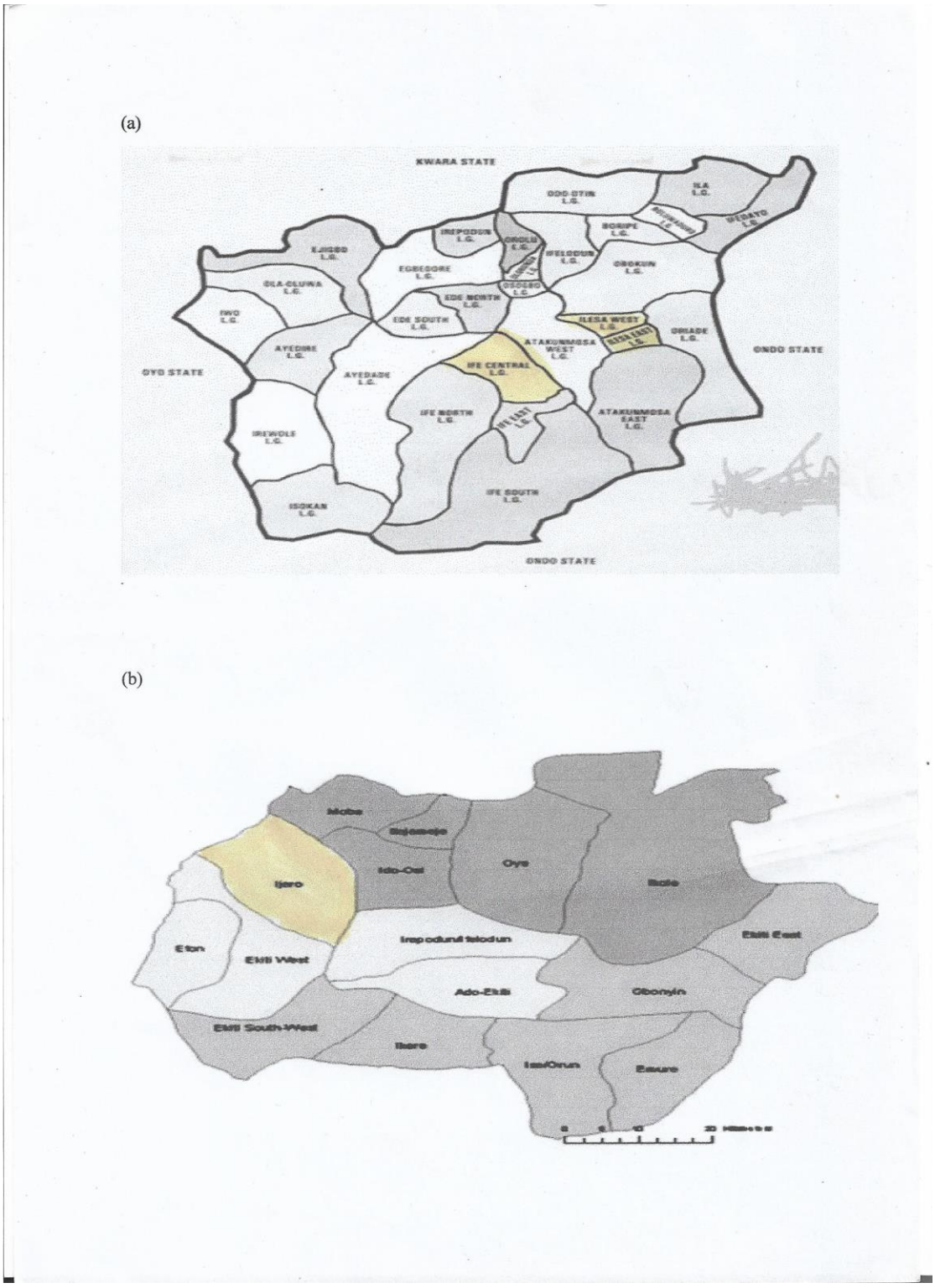


Figure 5-1: Maps showing the location of soil sample collection in Nigeria (a) Ilesha and Ife; (b) Ijero

The soils collected in transient at each location was thoroughly mixed together before they were amended with metals to mimic soil contamination. Certain soil properties such as pH, organic matter, particle size, cation exchange capacity, extractable metal content were investigated for each of the soil samples. For each of the soil to be used, two sets of 1500g was measured out and spiked with two different concentration of the metals solutions at a ratio of 10ml:100g to get the final metal concentration of 100 mg Pb/kg, 100 mg Cu/kg, 5 mg Cd/kg; 300 mg Pb/kg, 300 mg Cu/kg and 15 mg Cd/kg in the soils.

The metal solution was added to soil drop by drop and thoroughly mixed together to prevent (local) high concentration in some portion of the soil due to inadequate mixing. The soils were then left for 7 days before treatment with *Delonix regia* or biochar. At the end of the incubation periods, each soil was divided into three parts of approximately 500g each and two parts were treated with either 2% biochar or powder obtained from *Delonix regia* pods and while the third part without any treatment was used as control samples. After the treatments were applied, each of the samples were watered every four days to 10% of its water holding capacity in Table 5.1.

5.2.2.2 pH adjustment

In order to cover a wider pH range than what was obtained originally in the soil samples, two soils were treated with 1% Nitric acid to adjust their pH before their amendment were done. After 3 days of pH adjustment, pH 3.34 and 4.31 were recorded for the soils.

5.2.2.3 Organic matter adjustment

The collected soils were all very low in organic matter content, to investigate the effect of organic matter in the remediation process, the chosen soils were treated with humic acid at 2% (w/w). Humic acid (30.44g) was dissolved in 150mls of milli-Q water and kept for three days before it was applied to 1500g of soil. Two soils of different pH (4 and 6) were used for this purpose.

5.2.2.4 Measurements of soil organic matter, pH and CEC

The organic matter (%OM) of the soils were measured as loss on ignition by weighing 2g of air dried soil in a pre-weighed crucible and oven dried at 105^{o}C for 2hours before it was transferred into the muffle furnace where it was heated at 400^{o}C overnight. The samples were then cooled in a desiccator and weighed. The %OM was estimated as the mass difference between the initial and final sample weights divided by the initial sample weight multiplied by 100%.

Milli-Q water of 20 ml was added to 10g of air dried soil in 50ml polyethylene beakers. The mixture was stirred vigorously for 5 minutes on a magnetic stirrer and then allowed to settle for 1hour. The pH values were measured using a pH meter, model PHM 220, calibrated with buffers pH 4.0 and 7.0.

In order to determine the cation exchange capacity (CEC) of the soils, 4g of air-dried soils were weighed into centrifuge tubes and 30 mls of 1M sodium acetate solution was added. The mixtures were shaken for 10 minutes on an end-over-end shaker and centrifuged at 3000 revolution per minute for 5 minutes. The supernatants were discarded, the process was repeated one more time after which 30mls of 30% methylated spirit (IMS) was added (twice) to the residue in the tube to wash off any

unattached Na. The tubes were shaken for 5minutes, centrifuges and the IMS decanted. The attached sodium is leached off the soil by adding 30 ml of neutral 1M ammonium acetate to the residue in the tube, the tubes were shaken again for 10 minutes and centrifuged at 3000 rpm for 5minutes. The supernatants were filtered into 100ml volumetric flask and made up to the mark with 1M ammonium acetate. The solutions were used to determine the CEC using Corning 140 Flame photometer at compressor pressure 11psi (Lu, 2000).

5.2.2.5 Exchangeable metal content

Determination of the exchangeable metal content in the soils was done by using 0.01M $CaCl_2$ solution. For this procedure, 20 mls of 0.01M $CaCl_2$ was added to 2g of soil in centrifuge tubes and shaken on a shaker for 3 hours. The tubes were centrifuged at 4500 revolution per minute for 5 minutes. Then a 1.5 ml aliquot was pipetted into clean centrifuge tubes and centrifuged again at 6000 revolution per minute for 5 minutes. Finally, an aliquot was diluted a thousand times with 0.1M HNO_3 and the metal concentrations were analysed by ICP-MS.

5.2.2.6 Maximum water holding capacity

Plant pots were filled with 20g soil and watered until the water starts to drip from the bottom of the pot. The pots were covered and left to stand for 24 hours after which certain quantity (10g) were weighed into crucibles with known weight. The crucibles and contents were oven dried at 105^{o}C for 24 hours, allowed to cool and the dried weight of the soil samples were used to calculate the % maximum water holding capacity (equation 5.1) for each soil samples.

$$\%\ maximum\ water\ holding\ capacity = \frac{(wet\ weight - dry\ weight)}{dry\ weight} * 100\% \ldots\ldots \text{ Equation 5-1}$$

5.2.2.7 Particle size analysis

Soil of 20 g was weighed and mixed thoroughly with 200 ml of a solution containing 100 ml of 10% Calgon solution and 100 ml MQ water. The suspension was transferred into a 1000 ml measuring cylinder and made up to the mark with MQ water. The suspension was left to settle at room temperature and then stirred thoroughly with a plunger; at the end of the last stroke of the plunger the hydrometer was gently lower down into the suspension and timing began. At 32 seconds, a density reading (in g/cm^3) was recorded and at 8 hours another reading was taken without disturbing the system by stirring.

After the 8 hours reading was recorded, the supernatant clay suspension was gently poured off and the soil sludge made up to the mark with MQ water. The suspension was stirred and allowed to settle for 32 seconds and the suspension decanted off again. The process was repeated three times in all to ensure that all the silt and clay particles were removed from the cylinder leaving the sand portion. The remaining sand was transferred into a pre-weighed 200 ml beaker, oven dried at 105^{o}C for 48 hours and weighed; the difference in weight is the sand fraction of the soil. Density measurements were converted to weights and from these, the soil fractions were calculated as follows:

Silt: Density reading at 32 seconds (g/cm^3) - density reading at 8 hours (g/cm^3);

Clay: Density reading at 8 hours (g/cm3);

Sand: Difference in measured weighed.

The soil fractions were converted to soil texture using a soil triangle that was generated by the Soil Survey of England and Wales Classification.

5.3 Results and Discussion

5.3.1 *Soil properties*

The texture of the soils is similar as they were collected from the same region. They are all low in organic matter. All soils have pH values are below 7 and three of them are below or close to 5.5.

The pH range of all the soil samples in this work is slightly acidic (5.20 to 6.72) probably because of the mining activities undertaken on the soil. The more organic matter a soil has, the more functional groups available for complexation with heavy metals and thus more retention. The organic matter of the soil in this study are extremely low in the range of 0.02 to 0.03%, this might be because of land use. The sampling locations are areas where illegal mining operations are carried out and there is no agricultural activities or vegetation cover on the top soil.

The CEC of any soil assist in explaining its retention capacity for many metals. The more the CEC the more the available sites for exchange. CEC of the soils in this work are generally poor with values from 1.43 to 25.22 me/100g soil. Ilesha soil has 25.22 me/100g soil as CEC probably because the location was used for cocoa planting before the miners discovered gold in the soil.

The soil particle analysis revealed that about 58.2 to 64.72% of the soil particle size are sand. This have a direct impact on the low water holding capacity of the soil

samples, it is within 24.34 and 36.02%, soils having more particle sizes in the silt and clay portion have higher water holding capacity.

Extractable metal ions: The Extractable metal ions concentration of the soils are low (with the exception of cadmium in Ijero and Ekiti soils) due to leaching from the topsoil. It is expected of any soil possessing the above properties to have low extractable metal concentration. Shown in Table 5.1 are the properties of the soils.

Table 5-1: Properties of tropical soils used in this study

Soil Samples	Longitude	Latitude	pH	% OM	Particle size				CEC (me/100g soil	Water H. Capacity	Extractable Metal Content (mg/kg)		
					Sand	Silt	Clay	Texture			Cd	Cu	Pb
IJERO	5.0742	7.8139	5.20	0.018	64.72	17.5	17.78	Sandy loam	1.43	24.34	15.3	BDL	52.6
ILESHA	4.65	7.5333	6.72	0.033	59.62	12.5	27.88	Loamy sand	25.22	32.73	1.9	BDL	5.3
EKITI	5.0742	7.8139	5.40	0.026	58.2	15	26.8	Sandy clay loam	10.65	36.02	5.3	BDL	71.3
IFE	4.5667	7.4667	5.65	0.018	61.94	10	28.06	sandy clay loam	15.27	31.93	1.3	BDL	2.1

5.3.2 *Aging effect on remediation*

The concentration of metals obtained after analysis with the ICP-MS was used to calculate the efficiency of each of the treatment types shown in equation 5.2 on each sampling day during the incubation period.

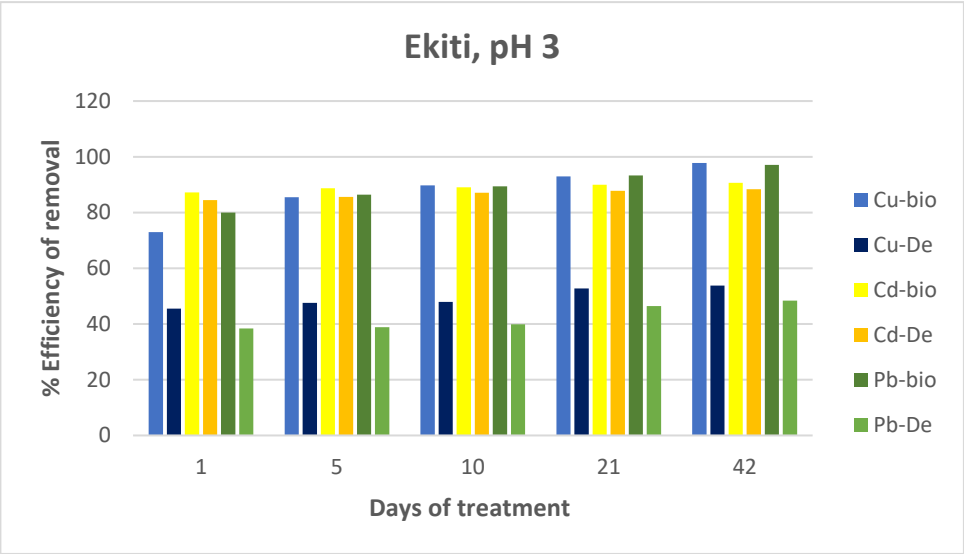
$$Efficiency\ of\ of\ removal\ by\ each\ treatment = {}^{C_a}/_{C_c} \quad \text{.....Equation 5-2}$$

where C_a is the difference available concentration between the control samples and the treated samples while C_c is the available concentration in the control sample.

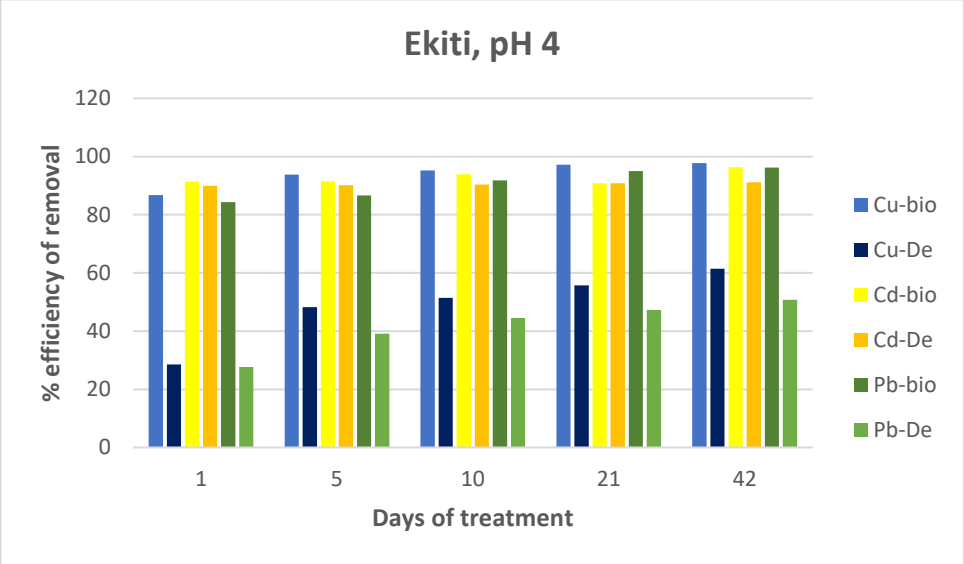
As much as possible, laboratory tests should mimic the most realistic situation, but freshly spiked soils do not allow the equilibration time that is required to resemble common field situation, thus aging is an important issue to consider in the assessment of metal-contaminated soils so that the result obtained could be more realistic (Lanno et al., 2004).

Five soil samples were studied to investigate the effect of aging on each of the remediation efficiency of each of the treatment materials; the results obtained are shown in Figure 5.2(a-e).

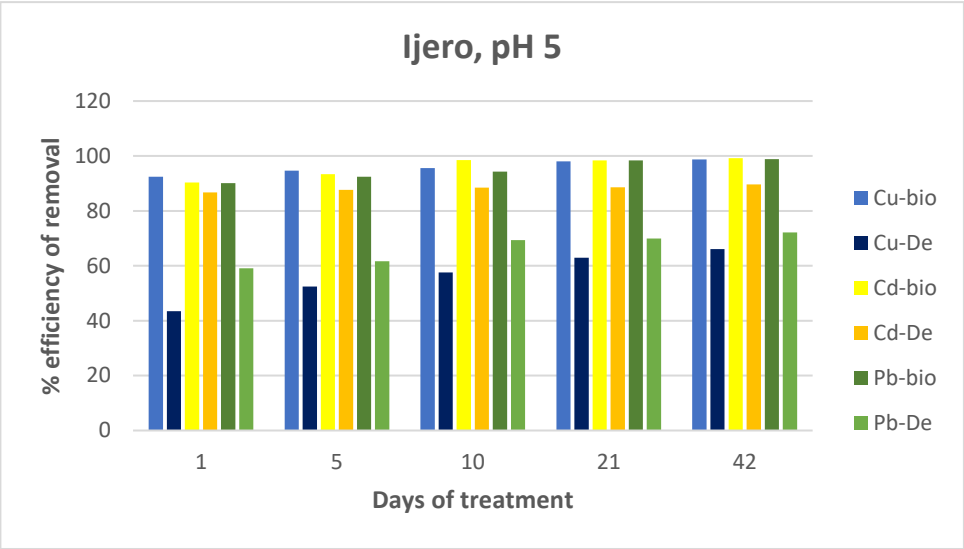
(a)


Ekiti, pH 3
% Efficiency of removal
120
100
80
60
40
20
0
1
5
10
21
42
Days of treatment
Cu-bio
Cu-De
Cd-bio
Cd-De
Pb-bio
Pb-De

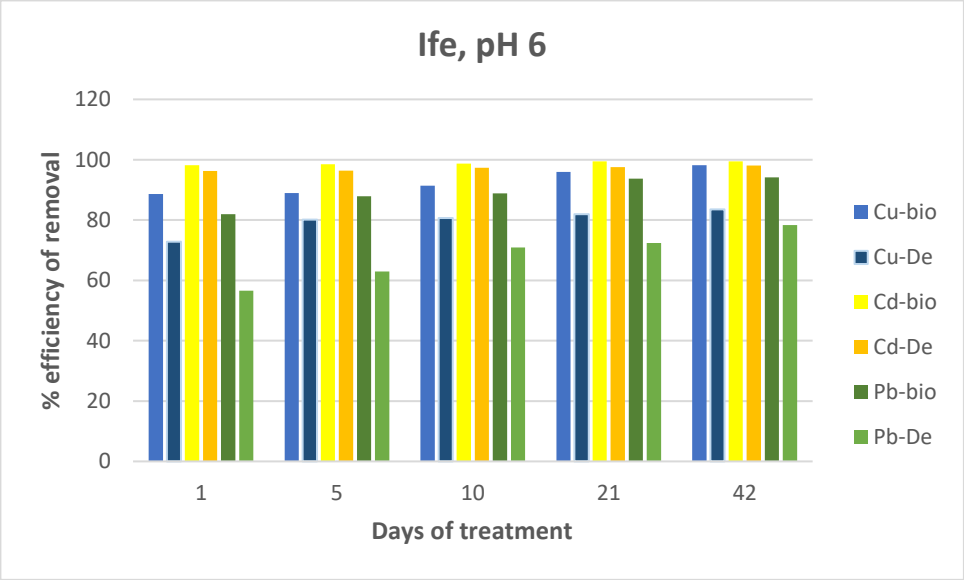
(b)


Ekiti, pH 4
% efficiency of removal
120
100
80
60
40
20
0
1
5
10
21
42
Days of treatment
Cu-bio
Cu-De
Cd-bio
Cd-De
Pb-bio
Pb-De

(c)


Ijero, pH 5
% efficiency of removal
120
100
80
60
40
20
0
1
5
10
21
42
Days of treatment
Cu-bio
Cu-De
Cd-bio
Cd-De
Pb-bio
Pb-De

(d)


Ife, pH 6
% efficiency of removal
120
100
80
60
40
20
0
1
5
10
21
42
Days of treatment
Cu-bio
Cu-De
Cd-bio
Cd-De
Pb-bio
Pb-De

(e)

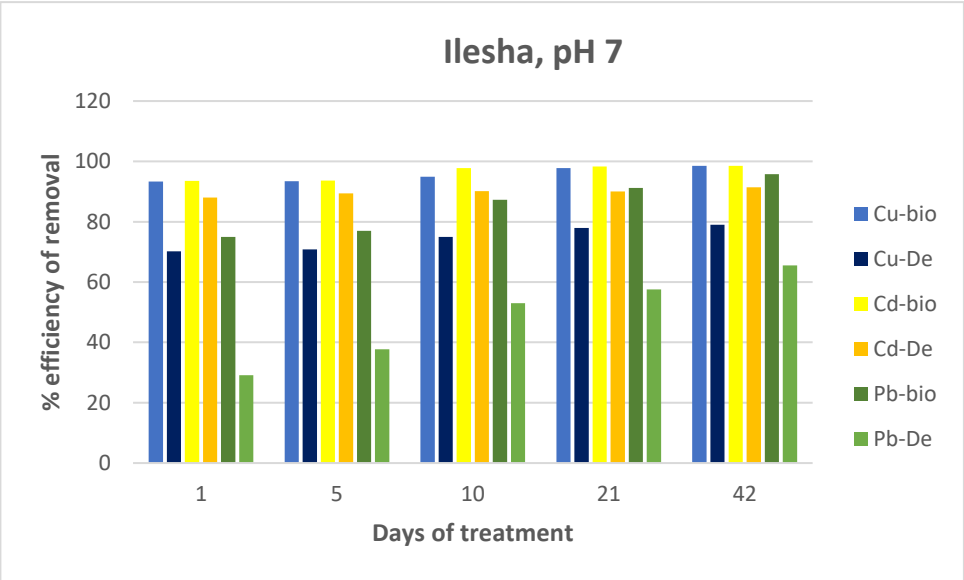


Figure 5-2(a-e): Effect of contaminant aging on the efficiency of 2% (w/w) Biochar and 2% (w/w) *Delonix regia* for the removal of copper, lead and cadmium from soils contaminated with Cu, Cd and Pb by for the incubation period.

The result for Ekiti soil with pH 3.4 shown in Figure 5.2a revealed that the removal efficiency recorded for copper and lead with both biochar and *Delonix regia* treatments were increasing as the treatment days (aging) increased, although biochar efficiency almost doubles the values for *Delonix regia*. The efficiency of the soil treated with *Delonix regia* did not change significantly for copper and lead until the twenty first day. This means that the adsorption of metals onto the soil solid phase was getting stronger with aging and it is easier and more efficient to remove them from the soil solution to reduce the available concentration of metals.

Cadmium immobilization efficiency was constant for both treatment irrespective of the sampling day and the values for both treatments were 87 to 90% and 85 to 88% for biochar and *Delonix regia* respectively.

Copper and lead removal by *Delonix regia* was moderate (50%) and increased with aging. The removal efficiency of the biochar treatment for copper and lead was high (>80%) from the start and on the increase as the aging of the treatment increased on Ilesha soil with pH 4 as seen in Figure 5.2(b), the removal efficiency of cadmium was high from the start of the experiment and remained unaffected with aging irrespective of the treatment used. A similar observation that aging had no effect on the availability of cadmium has also been reported (de Barros Amorim et al., 2005). In Figure 5.2(c) is the result showing the aging effect of treatment types on Ijero soil (pH 5), the efficiency for all metals was increasing with age of treatment for both types of treatment except for cadmium on *Delonix regia* which remained unchanged with aging period; cadmium on biochar which increased for the first three sampling days and then remained constant.

On Ife soil shown in Figure 5.2(d), there was slight increase in the removal efficiency for copper with aging on *Delonix regia* while no significant increase was noticed until (day 10) for copper on biochar treatments. Aging effect showed that no increase was observed for cadmium on both *Delonix regia* and biochar treatments whereas, in the case of lead, significant increase occurred from the first sampling day and all through the experiment for both treatment types. On Ilesha soil, the efficiency of both treatments increased on day 21 of treatment for the immobilization of copper and lead but for cadmium slight increase was observed from (day 10) when biochar was applied whereas aging had no effect on the removal efficiency of cadmium when *Delonix regia* was used as treatment as revealed in Figure 5.2e.

The results obtained from this work revealed that the efficiency of removal of *Delonix regia* for copper and lead was moderate (about 60%) and on the increase with aging while copper and lead removal efficiency was very high (above 90%) and increased

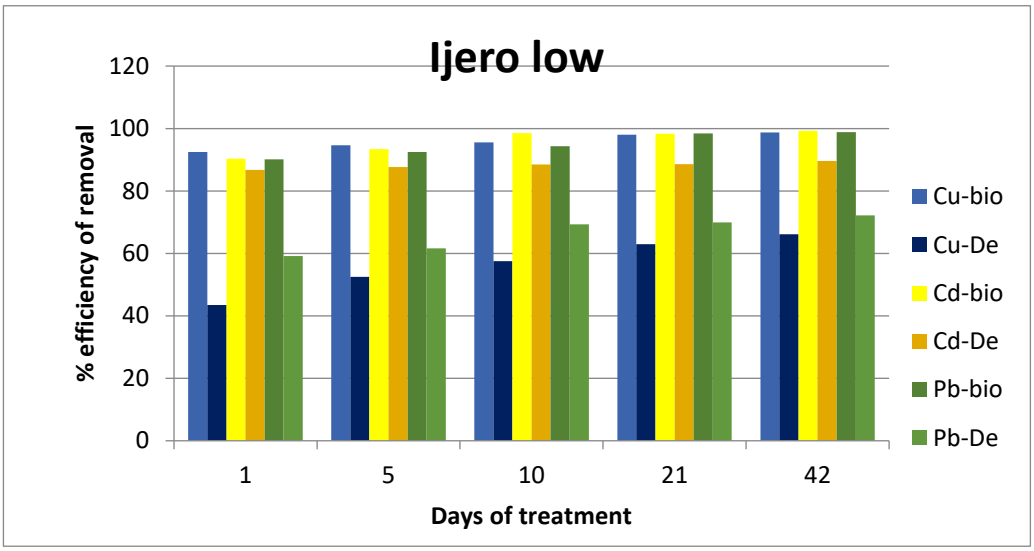
with aging on biochar amended soils whereas aging had no effect on the removal efficiency of cadmium on both treatment types. The study showed that more metals were being adsorbed onto the treatment materials as incubation period is increased. Biochar is more effective than *Delonix regia* but they could both be used on soils contaminated with these metals.

Overall, the above results have shown that in the soils amended with biochar and *D.regia* the efficiency of removing available metal fractions increased with aging for copper and lead whereas with cadmium efficiency of removal was constant. These indicate that it is more efficient and effective to remediate contaminated soils after a few weeks of the incident occurred rather than treating the soils immediately.

5.3.3 *Effect of different concentrations of metal ions*

The effect of different concentration of contaminants on the treatment were studied using two different concentrations (a low concentration of 100 mg/kg of lead and copper; 5mgCd/100kg which is the maximum allowable limits for the metals in agricultural soils and a high concentration of 300 mg/kg of lead and copper; 15mgCd/100kg, i.e. three times the allowable limits). Three sets of soil samples (Ijero, Ife and Ilesha soils with approximate pH 5, 6 and 7 respectively) were contaminated with these different concentrations. The results obtained from the study of different concentration of metal on removal efficiency is presented in Figure 5.3 to Figure 5. The result obtained in this study for Ijero soils are presented in Figure 5.3 (a-b).

(a)



(b)

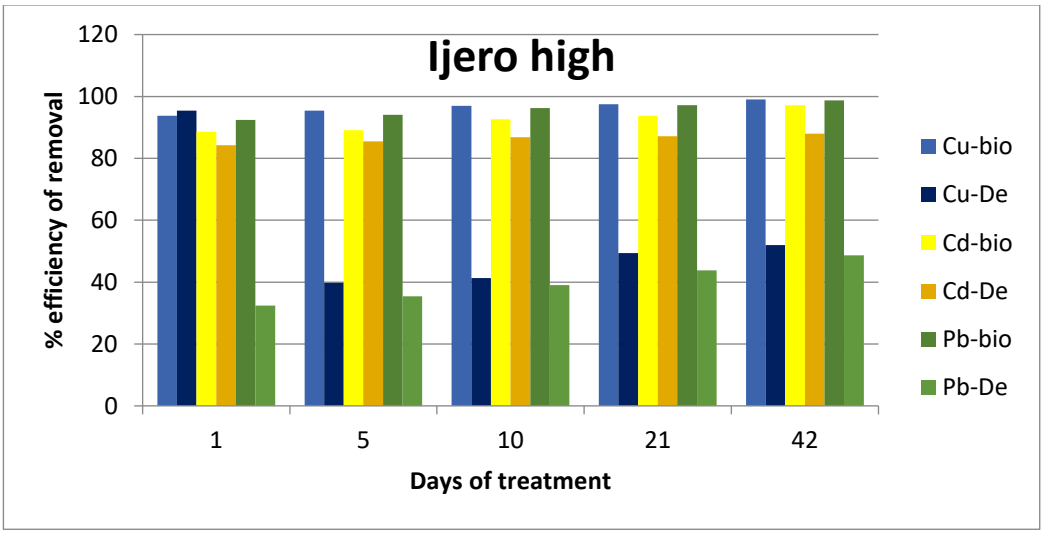


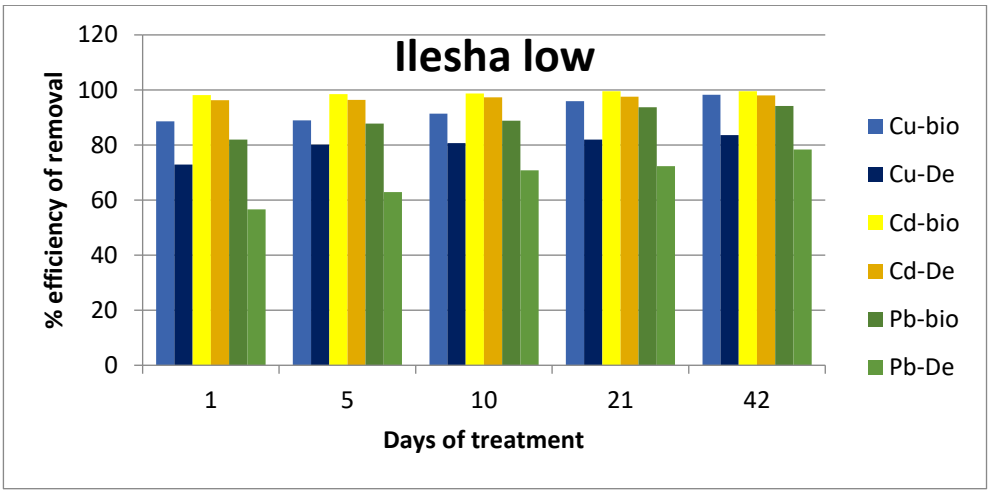
Figure 5-3 (a-b): Effect of heavy metal concentration on the efficiency of 2% (w/w) Biochar and 2% (w/w) *Delonix regia* for the removal of Cu, Cd and Pb from soils contaminated with Cu, Cd and Pb for the incubation period (a): low concentration of contaminants (b): high concentration of contaminants.

The results for Ijero soil in Figure 5.3 showed high efficiency for biochar on all the metals investigated throughout all the aging periods. The efficiency determined at both the high and the low concentrations were similar. The results indicate that biochar is a very efficient material for removing metals.

The case was different for the extractable metal when *Delonix regia* was used. A reduction in efficiency was observed in the soil with high concentrations of the metals than in the soils with low concentrations, with the exception of copper. In soil with high concentration, a significantly high efficiency of copper removal by *Delonix regia* was observed, though this might be due to experimental error. The observed reduction in efficiency with high concentration for lead and cadmium might be due to insufficient strong sorption sites on the *Delonix regia*.

The results obtained on Ilesha soil are shown in Figure 5.4 (a-b).

(a)



(b)

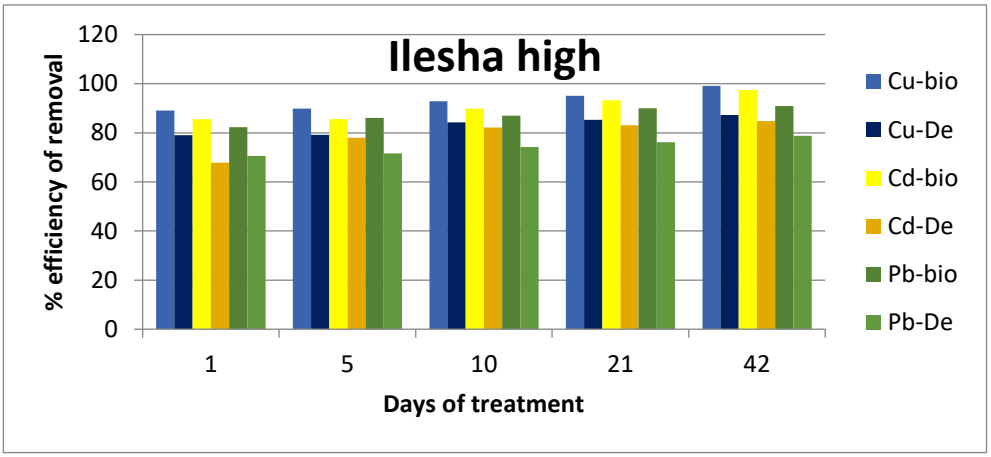


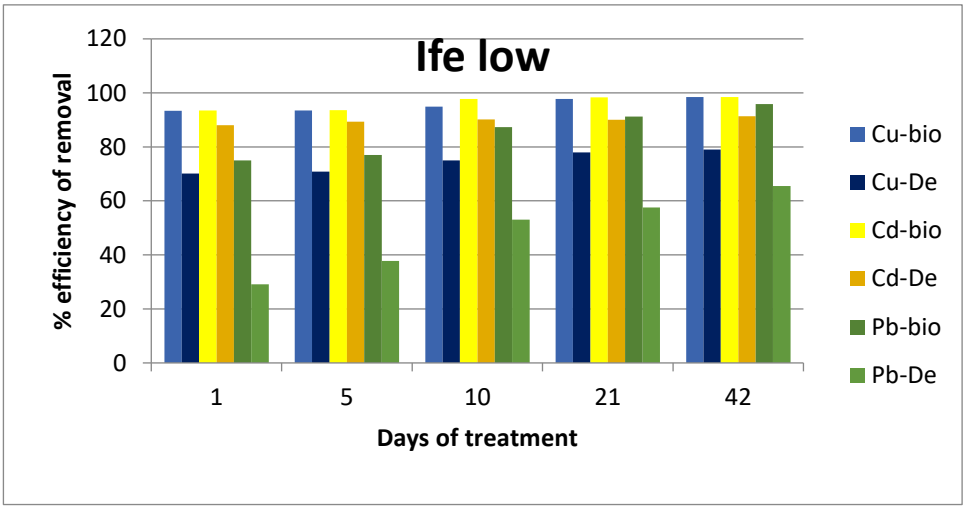
Figure 5-4(a-b): Effect of heavy metal concentrations on the efficiency of 2% (w/w) Biochar and 2% (w/w) *Delonix regia* for the removal of Cu, Cd and Pb from soils contaminated with Cu, Cd and Pb for the incubation period (a): low concentration of contaminants (b): high concentration of contaminants.

The efficiency for copper and lead removal by *Delonix regia* was slightly higher in soil with the high metals concentration than in the soil with low concentration. For cadmium, the treatment was more effective in soil with low metal concentration and it could be explained by the high CEC of the Ilesha soil.

The initial concentrations of the copper and lead had no appreciable effect on their removal efficiency when biochar was applied as treatment to the soils; cadmium removal efficiency by biochar was greater in soil with low initial concentration.

For Ife soils, the result of the study of the effect of different initial concentration of metal is presented in Figure 5. (a-b).

(a)



(b)

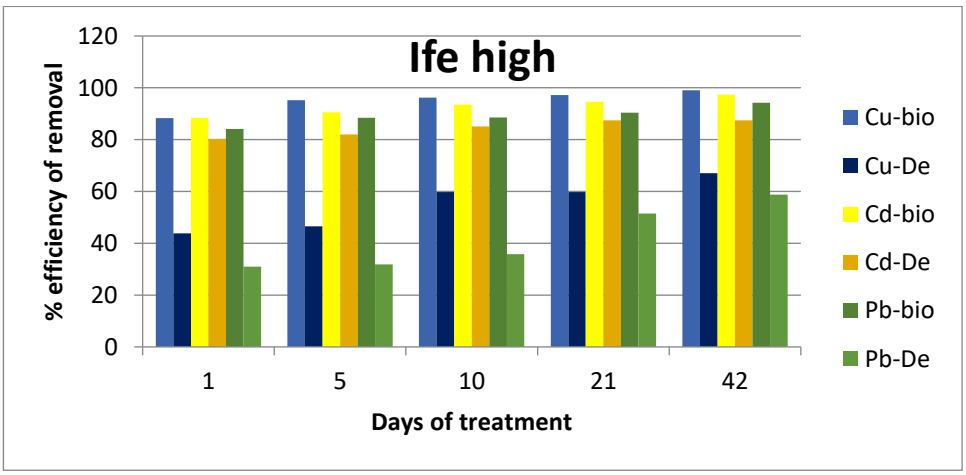


Figure 5-5(a-b): Effect of heavy metal concentrations on the efficiency of 2% (w/w) Biochar and 2% (w/w) *Delonix regia* for the removal of Cu, Cd and Pb from soils contaminated with Cu, Cd and Pb for the incubation period. (a): low concentration of contaminants (b): high concentration of contaminants.

For Ife soil with *Delonix regia* treatment, all the metals showed higher removal efficiency when the contamination level was lower (Figure 5.5). For biochar

treatment, initial concentration did not affect the removal efficiency significantly for all metals.

Removal efficiency of *Delonix regia* for all the metals varied from soil to soil when different concentrations were used; but generally average higher removal efficiency of 70% was recorded in the low level contaminated soils while 50% was achieved in the highly contaminated soils. Concentration difference had no effect on the removal efficiency of all investigated metals in biochar treated soils except in Ilesha soil where cadmium removal efficiency was favoured by 15% in the sample with low contaminant level. Biochar efficiency of removal is not affected by increasing the concentration of studied pollutants; thus, it would be suitable to use in both low and highly metal contaminated soils but the use of *Delonix regia* would be restricted to soils contaminated with low level of contaminants.

In the three sets of soils used in this study, different trend was observed in the efficiency of the applied treatments in low and high concentration owing to different properties of individual soil. Basically, remediation of soil treated with *D.regia* gave better efficiency in the low contaminated soils while with biochar amendment pollutants concentration have no significant effect on treatment effectiveness.

5.3.4 *Effect of soil pH on remediation process*

The pH of a soil is a singular measurement that can give many information that can be used to determine the characteristics of a soil. From soil pH values, an estimation can be made of the toxicity of some elements and the availability of essential nutrients in soils based on the knowledge of their relationship with pH (Thomas, 1996). Effect of soil pH on heavy metal removal are presented in Figure 5.6 to 5.11. The effect of soil

pH on removal efficiency of heavy metals by *Delonix regia* from polluted soils are shown in Figure 5.5.

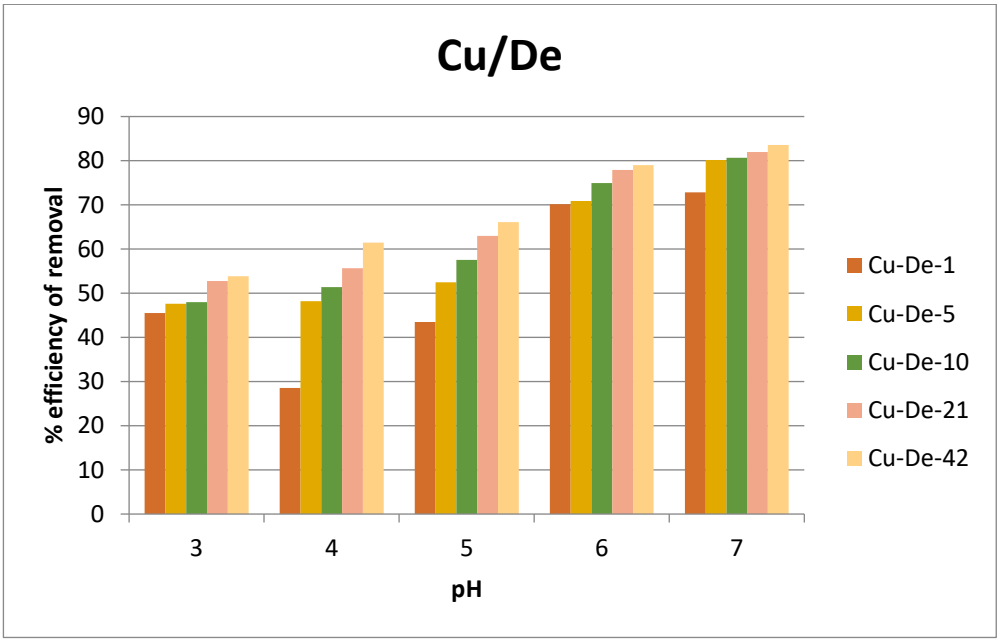


Figure 5-6: Effect of soil pH on the removal efficiency of Cu using 2% (w/w) *Delonix regia* in soils contaminated with Cu, Cd and Pb for the aging time up to 42 days.

At pH 4 and 5, moderate removal of about 65% extractable copper was achieved at day 1 of the contamination showing the least removal percentage. More than 70% of the labile copper was removed by *Delonix regia* throughout the entire period at pH 6 and 7. Increase in soil pH to 7 resulted in increased percentage removal of copper to 80%. The low sorption observed at pH 3 was due to proton competition for active sites (Rieuwerts et al., 2006); meaning that an increase in hydrogen ion concentration affects the mobilization intensity of heavy metals. Mobility of metallic elements in soils with neutral or alkaline pH is much lower than in highly acidic soils. It's been reported that the mobility of metals in soils with low pH decreases in the order: Cd> Ni> Zn> Mn> Cu> Pb (Fijałkowski et al., 2012).

The result in Figure 5.6 represented the removal efficiency of biochar for copper. It showed that all the soils treated with biochar, irrespective of the pH values, had high sorption for copper with the removal efficiency greater than 70% for all aging period up to 42 days.

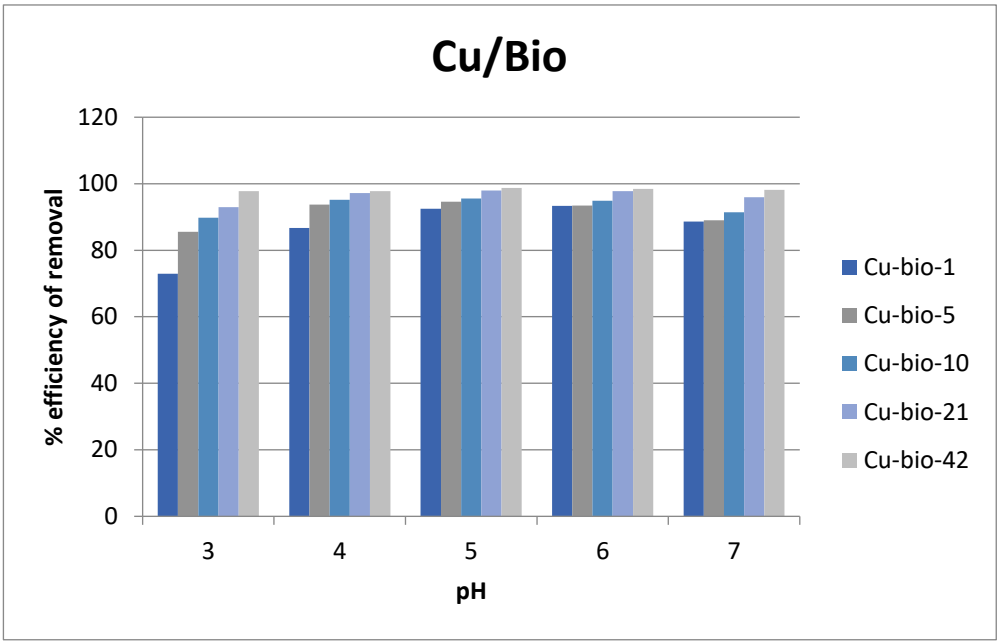


Figure 5-7: Effect of soil pH on the removal efficiency of Cu using 2% (w/w) Biochar in soils contaminated with Cu, Cd and Pb for the aging time up to 42 days.

Soil pH values seemed not to have significant impact on the efficiency of biochar treatment because the use of biochar as amendment increased the pH of each of the soil samples by a factor; thus, the pH 3 was invariably at pH 4 because of the addition of biochar.

The removal efficiency of cadmium by *Delonix regia* from contaminated soils presented in Figure 5.8 revealed that *Delonix regia* is able to remove cadmium irrespective of the soil pH.

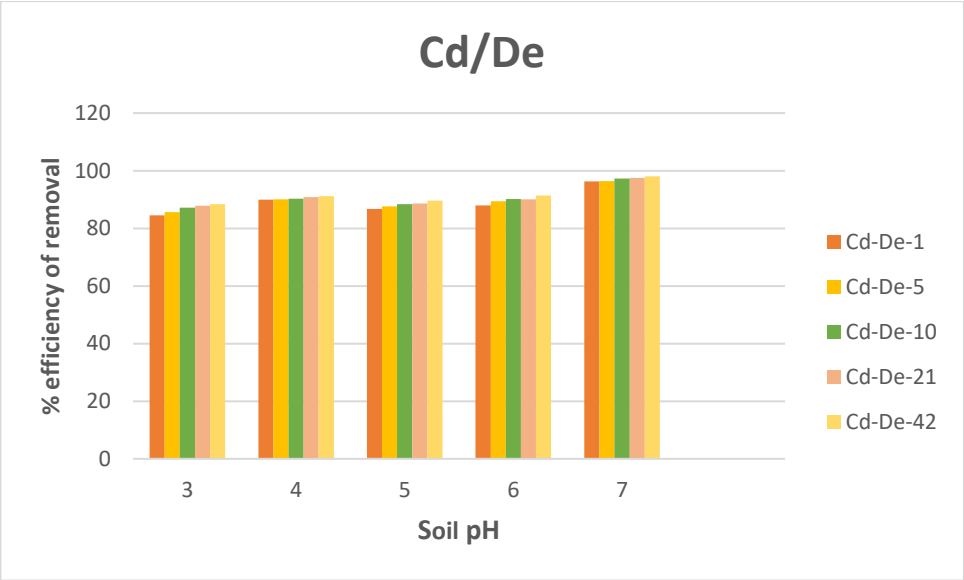


Figure 5-8: Effect of soil pH on the removal efficiency of Cd using 2% (w/w) *Delonix regia* in soils contaminated with Cu, Cd and Pb for the aging time up to 42 days.

The removal efficiency was higher than 80% even at day 1 of the soil contamination. There was a slight increase with time. It was reported by Kabata-Pendias (2004) that metal bioavailability is reduced in neutral soil. The high removal efficiency for Cd at pH 7 observed in Figure 5.8 above, >95% at day 1, indicates that its bioavailability is reduced significantly under the treatment.

The results for the effect of pH on the removal efficiency of cadmium using biochar is shown in Figure 5.9.

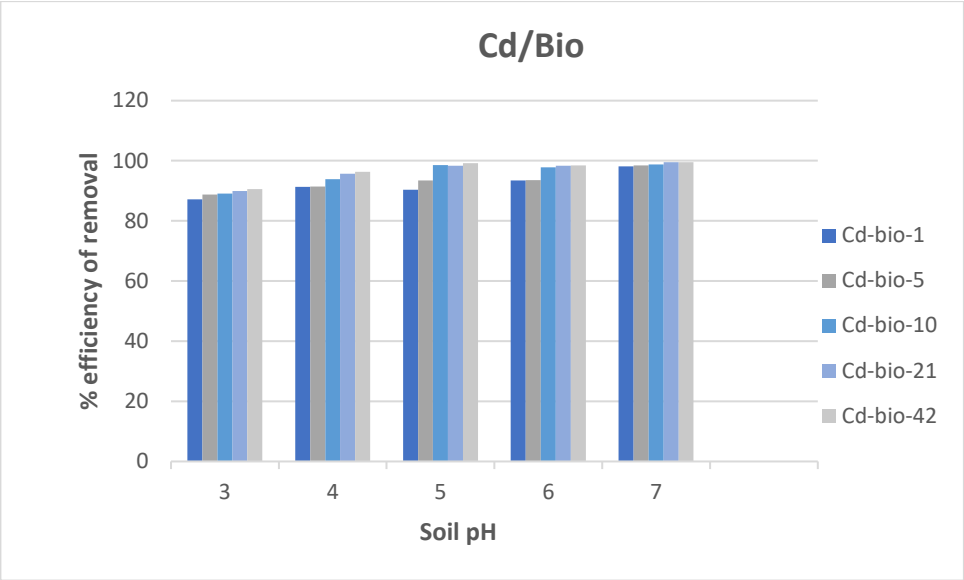


Figure 5-9: Effect of soil pH on the removal efficiency of Cd using 2% (w/w) Biochar in soils contaminated with Cu, Cd and Pb for the aging time up to 42 days.

The results in Figure 5.9 for the removal efficiency of cadmium by biochar showed high removal efficiency of > 86% for all soil pH considered, with nearly 100% removal for soil pH greater than 5. The result presented in Figure 5.10 represent the effect of pH on the removal efficiency of lead using *Delonix regia*.

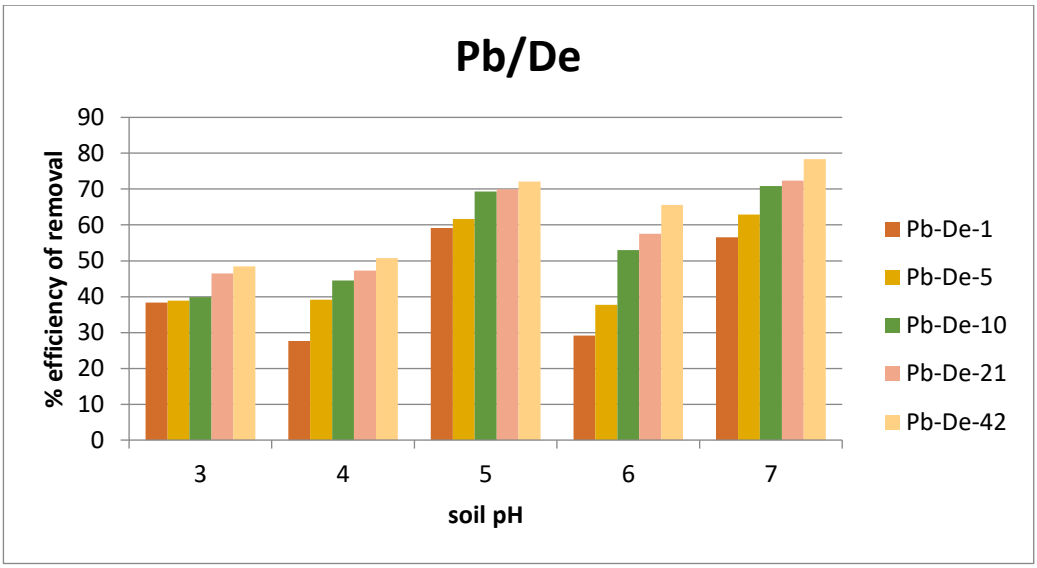


Figure 5-10: Effect of soil pH on the removal efficiency of Pb using 2% (w/w) *Delonix regia* in soils contaminated with Cu, Cd and Pb for the aging time up to 42 days.

Removal efficiency of lead by *Delonix regia* on varying soil pH shown in Figure 5.9 was moderate. Average highest percentage removal throughout the incubation period was observed at soil pH 5.

The effect of soil pH on the removal efficiency of lead using biochar is presented in Figure 5.10.

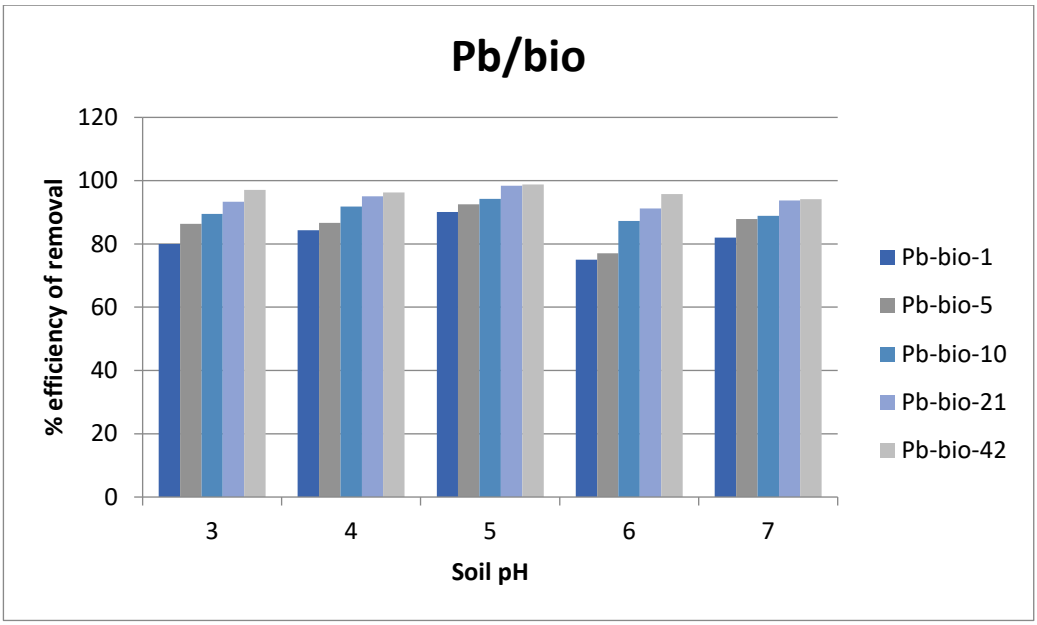


Figure 5-11: Effect of soil pH on the removal efficiency of Pb using 2% (w/w) hardwood biochar in soils contaminated with Cu, Cd and Pb for the aging time up to 42 days.

High removal efficiency of greater than 80% for Pb by biochar treatment in all tested soil pH values and throughout the aging period was observed (Figure 5.11). Similar to results obtained for *Delonix regia*, the best removal efficiency was obtained at soil pH 5.

The sorption of Cu, Cd and Pb were dependent on the soil pH. Lower sorption and consequently lower removal efficiency were observed in soils with low pH when *Delonix regia* was used. Addition of *D.regia* did not change the pH of the soil. However, in the case of biochar treated soils, all the soil pH values were increased by one unit. This increase in pH and stronger binding properties of biochar resulted in higher sorption of Cu, Cd and Pb in all soils treated with biochar. Consequently, high metal removal efficiency was observed for all the soils samples studied. Increasing soil pH resulted in increased Cd and Pb adsorption was also reported by Appel and Ma (2002).

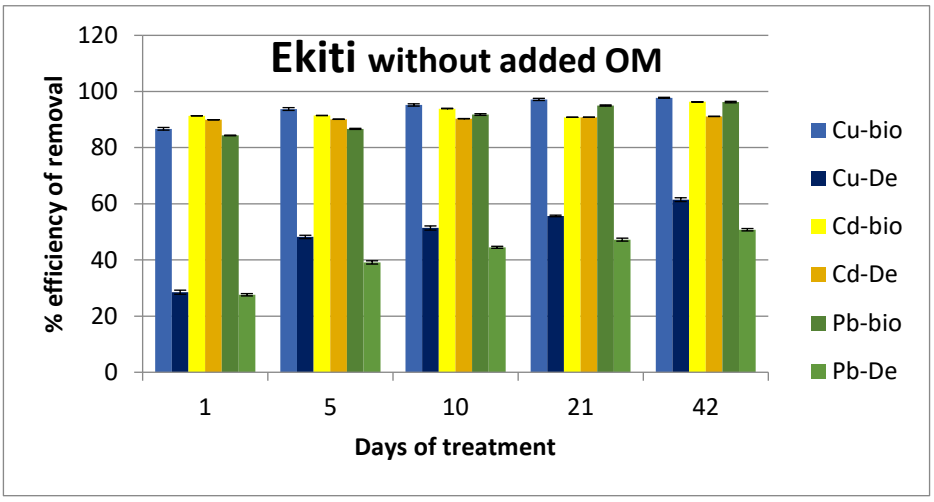
Delonix regia removal efficiency for lead was moderate (50%) and on the increase with pH increase; best average removal of (65%) is at pH 5; the efficiency of copper removal by *Delonix regia* increased gradually up to 80% with increase in soil pH to 7; for cadmium an average of 90% removal efficiency was recorded and *Delonix regia* seemed effective irrespective of pH. Biochar removal efficiency (average of 80% and 95%) for lead and copper respectively was high and increased with pH. Soil pH has no significant effect on the removal efficiency of cadmium in biochar amended soil. An increase in soil pH caused a resulting increase in the removal efficiency of the treatments for copper and lead. *Delonix regia* is better suited to soil pH of 5 to 7. Biochar efficiency of removal is not significantly affected by soil pH and will thus be a good treatment to use on any polluted soil without pH restraint especially in the highly acidic soil contaminated by heavy metal wastes.

5.3.5 *Effect of organic matters on remediation process*

The results obtained when efficiency of both types of treatment was investigated with the addition of humic acid particles as organic matter are represented in Figures 5.12 and 5.13.

This experiment was done using Ekiti and Ilesha soils at pH 4 and 6 respectively. The results of the effect of soil organic matter on the removal efficiency of metals by biochar and *Delonix regia* in Ekiti soils at different aging period is presented in Figure 5.12(a-b).

(a)



(b)

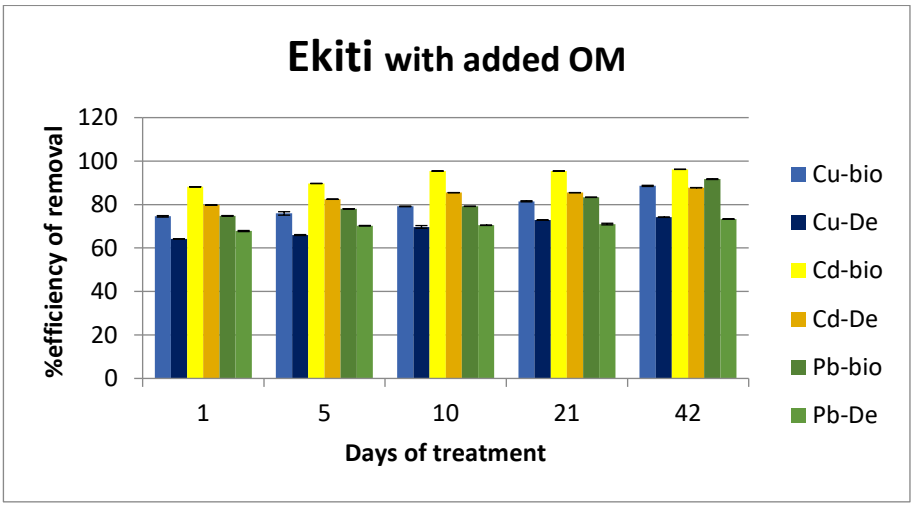


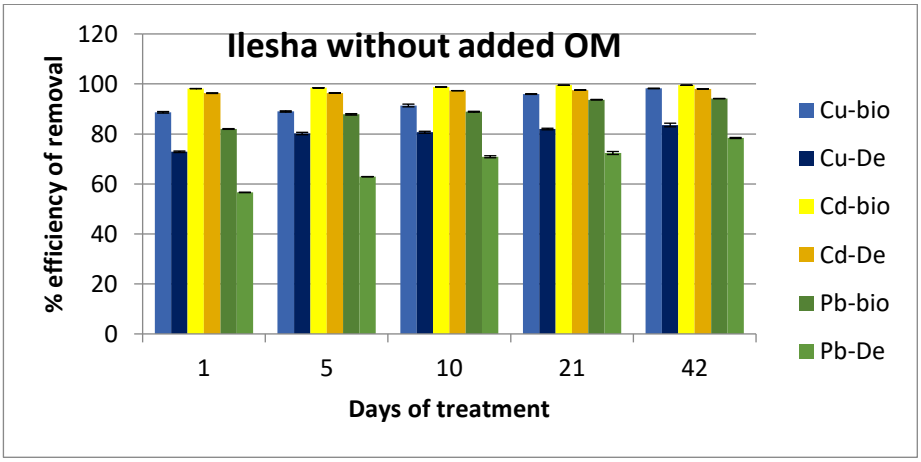
Figure 5-12(a-b): Effect of organic matter on the removal efficiency by 2% (w/w) Biochar and 2% (w/w) *Delonix regia* for Cu, Cd and Pb from soils contaminated for different aging period, (a): Ekiti soil without organic matter (b): Ekiti soil with organic matter.

As shown in Figures 5.12(a-b), the presence of organic matter in Ekiti soil increased the removal efficiency of *Delonix regia* for the remediation of copper and lead in all of the aging period, but its efficiency for the removal of cadmium was unaffected. Ma et al. (1983) reported that soils with high pH and high organic matter were able to retain more lead than those possessing lower values in these properties. When Ekiti

soil was amended with biochar, the removal efficiency was reduced for all the metals studied except for cadmium. This is probably due to i) organic ligands from humic acids preventing sorption of metals onto the soils or/and biochar and ii) the pH of the soil decreased after the addition of humic acid.

The results in Figure 5.13(a-b) are for Ilesha soil treated with humic acid particles to show the effect of organic matter on the removal efficiency of metals by biochar or *Delonix regia* from contaminated soils.

(a)



(b)

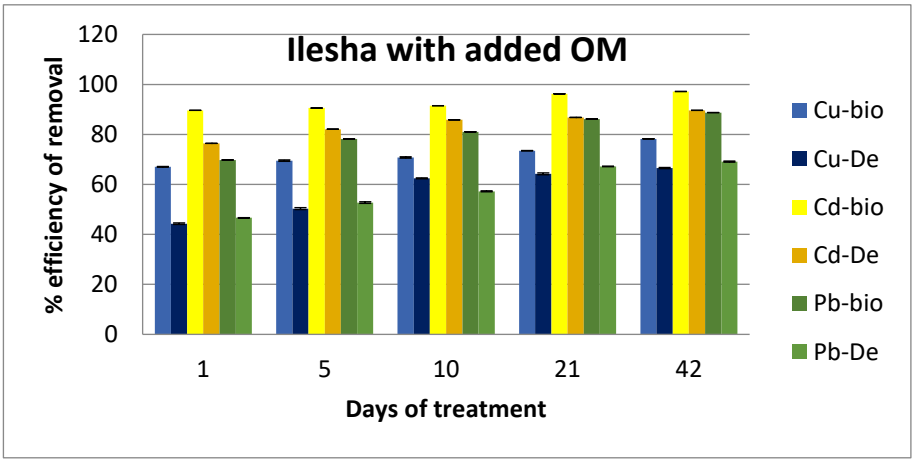


Figure 5-13(a-b): Effect of soil organic matter on the removal efficiency by 2% (w/w) Biochar and 2% (w/w) *Delonix regia* for Cu, Cd and Pb from contaminated soil of different aging period. (a) Ilesha soil without organic matter (b): Ilesha soil with organic matter.

The results of soil organic matter effect on the removal efficiency of metals by biochar or *Delonix regia* from contaminated soils using Ilesha soil presented in Figure 5.13(a-b) showed that similar results and similar trends as for Ekiti soil were observed, which further confirmed the finding of reduced removal efficiency of metals in the presence of high OM represented by humic acids.

The presence of added organic matter to the soils increased the removal efficiency of *Delonix regia* for copper and lead from 50% to 70% copper and 45% to 70% lead in Ekiti soil; the presence of organic matter did not affect the removal efficiency of cadmium in this soil; while in Ilesha soil treated with *Delonix regia*, the sample without added organic matter have moderate efficiency (an average of 50%) of removal for lead and a slight increase to 55% when organic matter was added.

Higher % removal for copper and cadmium (75% copper and 90% cadmium) were recorded in the soil without organic matter added and in the soil with organic matter removal efficiency of (58% copper and 86% cadmium) were recorded. For Ijero and Ilesha biochar amended soils, higher % removal efficiency was recorded for all metals in all the soils without added organic matter. The presence of OM enhanced the removal ability of *Delonix regia* for the metals; the *Delonix regia* material could be useful as treatment in soils rich in organic matter especially agricultural soils contaminated with low levels of contaminants; the opposite was observed in biochar treated soils, increased removal efficiency was recorded in soils without added organic matter. It thus can mean that biochar can be useful in removing metals from weathered and exposed soils.

5.4 Conclusion

Generally, from this chapter, *Delonix regia* removal efficiency was better at pH 5, in soils with added organic matter and at low pollutants concentration; its efficiency increased with aging and soil pH while for biochar, increasing aging time and soil pH increased the removal efficiency, efficiency is the same at both concentrations, but the influence of organic matter decreased its removal efficiency.

The removal efficiency of both types of treatment increased with aging, that is more metal were being adsorbed onto them as incubation period prolonged and they could both be used on soils contaminated with these metals although biochar is more effective than *Delonix regia*.

The studied concentration levels had no impact on the removal efficiency of biochar for all the considered metals, biochar would be suitable to use in both low and highly metal contaminated soils but *Delonix regia* would be considered a choice in soils contaminated with low level of contaminants.

Soil pH affected the removal efficiency of both treatment types except for cadmium where soil pH had no effect. Increasing soil pH within the range studied increased the removal efficiency of the treatments for copper and lead. *Delonix regia* is better suited to soil pH of 5 for lead; neutral pH for copper. Biochar has high removal efficiency at pH range between 3.40 and 6.72 and will thus be a good treatment to use on any polluted soil without pH restraint especially in the highly acidic soil contaminated by heavy metal wastes.

The presence of OM enhanced the removal ability of *Delonix regia* for the metals when soil properties such as CEC are too low; the *Delonix regia* material could be useful as treatment in soils rich in organic matter; the opposite was observed in

biochar treated soils, increased removal efficiency was recorded in soils without added organic matter. It thus can mean that biochar can be useful in removing metals from weathered and exposed soils like some in the mining areas.

Chapter 6. Assessment of metal availability and kinetics of resupply in remediated soils using DGT technique and DIFS model

6.1 Introduction

Soils serve as the major reservoir for heavy metals released into the environment as a result of human activities (Wuana and Okieimen, 2011). Their total concentration persist in soils for a very long time after they are introduced because they cannot be degraded by microorganisms (Adriano, 2001); though the chemical forms and bioavailability may change. Measurements of the total metal contents, after *aqua regia* digestion, of polluted soils are necessary to determine the potential risk of the soils, but only the soluble, exchangeable and chelated metal species in soils are the fractions available to plants (Kabata-Pendias, 1993). Limited methods are available that give information on the dynamics and mobility of heavy metals. Most of the efforts have been made on establishing correlations between metal fractions in soils and plant uptake (Alvarez et al., 2006) without great success.

The use of selective chemical extractions (single and sequential methods) is the usual approach for understanding the interaction of heavy metals with soil and sediments components, or for assessing heavy metals mobility and availability to plants (Beckett, 1989, Das et al., 1995). Single extraction procedures are utilised to evaluate the exchangeable fraction of metals in soils while sequential extraction are employed to assess the association of metals with different solid-phase components in sediments (Sahuquillo et al., 2003). Sahuquillo et al. (2003) reported considerable extraction of the most mobile elements (cadmium and zinc) with the use of $CaCl_2$, copper and lead showed higher extraction values with EDTA; while EDTA and acetic acid metal

extractability were reported to provide more information on the complexation and acidification processes.

Bakircioglu et al. (2011) compared the extractability of copper, manganese, nickel, lead and zinc in soils by both single and sequential extraction with (HCl, EDTA, DTPA, $CaCl_2$ and H_2O) and found the extraction capacity of the analysed metals to be in the order: HCl>EDTA>DPTA>$CaCl_2$>H_2O. On using simple correlation analyses, the result indicated that the extractable lead and nickel of soils by HCl, EDTA and DTPA were significantly correlated with the metal contents of wheat grains. For $CaCl_2$, H_2O and BCR extraction procedures there was a relatively poor correlation between the extractable metals of soils and the metal contents of wheat grains.

Under field-like conditions, Hooda et al. (1997) compared four extractants (DPTA, EDTA-$(Na)_2$, NH_4NO_3 and $CaCl_2$) in 13 soils on which wheat, carrots and spinach were grown to maturity. A comparison of cadmium, copper, nickel, lead and zinc contents in the edible portions of the plants and soil by all tests performed were found to be well correlated; the best predictor test was reported to vary across the metals and plants species studied.

Another approach to assessing the available metal in soil is through the direct and independent measurement of soil solution concentration since plants take up nutrient and contaminants mainly from the soil solution. The use of total dissolved metals in soils has gained recognition as a means of assessing bioavailability and toxicity of metals in soils because plants can only take up dissolved metals in the soil solution. In an experiment performed by Pavan et al. (1982) to investigate the presence of available Al on growth and mineral nutrition of coffee seedlings, soil solution chemical composition data was inputted in a computer program which chemically

speciated Al in the soil solution. The result obtained from the shoot and root correlated with KCl-exchangeable Al of soil.

All the measurements used in these reported works do not account for the ability of the soil to replenish solution after the extraction of metal; to be able to account for the dynamics of the soil/solute system, the diffusive gradients in thin films technique was proposed (Davlson and Zhang, 1994). The DGT has been developed to measure supply fluxes of metals in sediments (Zhang et al., 1995) and it has proven to be a very promising tool to assess both the kinetics of resupply and the bioavailability of metals to plants (Zhang et al., 2001).

Any method to be used to assess the availability of heavy metals should ideally be applicable with minimum disturbance of the soil without disrupting the physical-chemical equilibrium between the solid and solution phases (Zhang et al., 1998). The DGT technique is suitable in this regard because it allows in-situ determination of metal concentration to be carried out without disrupting the system (Zhang et al., 1998). Thus, DGT can be used as a powerful tool for assessing bioavailability of metals in soils , taking into account metal concentration in soil solution and the solid phase and at the same time providing useful information on the kinetics of release from the solid phase to solution (Gu et al., 2017). Bioavailability rather than total concentration of metal was used by Gu et al. (2017) to investigate the biological responses of *Eisenia fetida* to cadmium in soil. Concentrations of cadmium in soil solution, by $CaCl_2$ extraction and DGT measurement were carried out. Result obtained revealed DGT measurement to be a better index than soil total concentration in predicting the accumulation of Cd in earthworms.

Guan et al. (2017) employed the DGT technique in the assessment of the desorption of bisphenols (an organic contaminant), from soil and reported that based on the labile partition coefficient (Kd), most of the bisphenols in the soil could participate in the labile exchange (that is be released to the solution). They noted that, though the rate of bisphenol release was relatively slow, soils with more binding sites (due to the presence of higher DOM and CEC) could resupply bisphenols at a higher rate.

Song et al. (2018) assessed the environmental risks arising from pollution by using DGT measurement and sequential extraction procedures to quantify the labile pools of copper, iron, manganese and nickel in soils obtained from a site committed to industrial sludge treatment.

According to Zhang et al. (2001), it was concluded that DGT measurement could serve as a quantitative measure of bioavailable metals in soils. Copper measurements were obtained from DGT, soil solution concentration, by EDTA extraction and free Cu(II) activity in soil solution in 29 different soils and a comparison to its concentrations in the plant material of *Lepidium heterophyllum* grown on same soils were made. Results obtained from plant concentrations were linearly related and highly correlated to copper concentration from DGT measurements but were more scattered and nonlinear compared to free $Cu^{2}+$ activity, EDTA extraction or soil solution concentrations.

Aim and Objectives

In this chapter the aim is to carry out the risk assessment of soils, contaminated with lead, copper and cadmium, by using diffusive gradient in thin films technique before and after remediating the soils with biochar and *Delonix regia* material.

In achieving the aim, the following objectives were set:

(1) To assess the availability of metals in remediated soils through soil solution concentration C_{ss} and DGT measured labile concentration C_{DGT}.

(2) To investigate the resupply of heavy metals from the solid phase to soil solution using index of resupply, R values, and coefficient of distribution of the labile pool, K_d values.

(3) To assess the kinetics of resupply by response time, T_c and rate of desorption, k_{-1}; and

(4) To assess aging effect on index of resupply, R values, coefficient of distribution of the labile pool, K_d values and response time, Tc.

6.2 Materials and Methods

6.2.1 *Materials*

Acrylamide solution (40%) and DGT gel cross-linker (2%) were used to prepare gel solutions used for both the resin gels and the diffusive gels.

Ammonium persulphate (10%, 0.1 g in 1 g of water) (prepared daily) as initiator and N,N,N'N'-Tetramethylethylenediamine (TEMED), 99% as catalyst were used in gel preparation.

Ion-exchange resin (Chelex-100 mesh) was used to make the binding gel for the DGT device.

DGT moulds supplied by DGT Research Limited (Lancaster, UK), glass plates and spacers for setting up the DGT devices and making gels of the desired thicknesses.

Metal salts of copper chloride dihydrate, cadmium and lead nitrate, solutions prepared from these salts were used to (contaminate) spike the soils.

Tropical soils were used as samples for the remediation study.

Biochar from Bodfari Environmental, UK and *Delonix regia* pods are the materials added to the contaminated soils to immobilize the heavy metals.

Nitric Acid BDH Aristar Ultra was used for the elution of metals from the binding gel.

6.2.2 *Methods*

6.2.2.1 Chelex resins gels and diffusive gels for DGT Devices

All experimental apparatuses and DGT plastic moulds were acid washed in 10% nitric acid overnight and rinse properly with MQ water before use. The Chelex binding layer (Chelex-100, Bio Rad) and diffusive gels were soaked in 0.1M $NaNO_3$ solution before use while the filter membranes were soaked in MQ.

6.2.2.2 Preparation of gel solution

Gel solution of 100 ml was made by mixing 15 ml DGT gel cross-linker (measure by weighing 15 gram of the solution) and 47.5 ml MQ water (or deionised water) together in a clean plastic bottle (or beaker). The mixture was shaken and then 37.5 ml acrylamide solution (40%) was added. It was ensured that the gel solution is well mixed by adequate shaking before storing in the refrigerator for usage.

6.2.2.3 Diffusive gel preparation

An acid washed spacer of thickness 0.5mm was placed round three of the four edges of acid washed glass plates and clipped together with plastic clips, the glass plates were set in such a way that 1mm overlap of the edges were left without the spacer.

Gel solution of 10 ml was pipetted into a plastic container and 70 µl of ammonium persulphate solution followed by 25 µl of TEMED solution were added. The solution was mixed very well. The solution was pipetted in a smooth controlled fashion between two glass plates.

The assembly was left at about 42~46^{o}C for at least 1 hour until the gel had completely set and then prized opened. The gel was washed in ~1 litre of MQ water (or deionised water) first and then changed to another litre of MQ for hydration. After a few hours, the change was carried out again, total number of change water was between 3-4 times for 24 hours hydration. The gel was stored in 0.01M $NaNO_3$ solution until needed (Pelcová et al., 2014, Zhang and Davison, 1999).

6.2.2.4 Resin Gel Preparation

Chelex-100 mesh was soaked in MQ for at least one hour, the excess water was decanted off afterwards. Acid washed plates and spacers of thickness 0.25mm were set and clipped in such a way to permit easier pipetting of the gel solution.

Soaked Chelex resins (4g) was weighed into a plastic container into which 10ml of gel solution was added and the mixture was thoroughly mixed. 60 µl of ammonium persulphate solution and 15µl of TEMED were added afterwards and mixed vigorously ensuring that the resin beads were suspended in the mixture. This was pipetted in a smooth controlled fashion between the two glass plates and maintained at about 42 ~ 46^{o}C for at least 1 hour until the gel is completely set. The resin will settle on one side of the gel by gravity if laid flat during setting. After the gel has set the assembly was prized opened and the Chelex gel was hydrated in MQ water. The water

was changed 1~2 times, it was then stored in 0.01M $NaNO_3$ solution (Pelcová et al., 2014, Zhang and Davison, 1999).

6.2.2.5 Testing DGT Device Performance

The gels and filter membrane were arranged on the moulding base by placing the Chelex gel on the base first and ensuring the resin side is faced up. Then the diffusive gel was placed on top of the Chelex gel followed by the filter membrane. Carefully the cap was fittedensuring it is horizontal. Then an even force was applied to press it down to the bottom of the base.

An immersion solution containing 0.01M $NaNO_3$ with 10 ppb of Cd made by mixing 2 L of MQ water and 20 ml of 1M $NaNO_3$ solution and spiked an appropriate amount of Cd standard solution was poured into a 3L plastic container. The testing DGT units were placed in the immersion solution making sure the plane of the filter is vertical, parallel to the container walls and facing towards the centre of the container. The time and solution temperature were noted down, and the solution was well stirred for 4 hours.

An aliquot of the immersion solution was taken for analysis at the beginning of the experiment, temperatures and samples of the immersion solution were once again taken for analysis at 2 and 4 hours. The DGT units were taken out of the solution and the surface was rinsed with MQ water, the resin gels were retrieved after deployment by inserting a screw driver into the grove in the cap and twisting it. The Chelex resin gels were placed singly in clean 1.5ml centrifuge tubes and 1ml of 1M HNO_3 solution was added ensuring the resin gel is fully immersed in the HNO_3 solution overnight

before analysis. An aliquot was pipetted from the sample and diluted 10 times with MQ water before analysis by ICP-MS.

6.2.2.6 Soil amendment and treatment

The detailed procedure is explained in section 5.2.2.1, the same soil samples that were used in chapter 5 are the soil samples used in this chapter because this chapter focuses on the assessment of the contaminated soils that were treated with biochar and *Delonix regia.*

6.2.2.7 DGT deployment and retrieval

For the deployment of DGT devices, 100g soil samples were weighed into clean plastic beakers, and mixed with milli-Q water to get a soil moisture content of about 80% maximum water holding capacity of the soil. The amount of MQ water added to each soil sample of control, biochar and *Delonix regia* is shown in Table 6.1.

Table 6-1: Water added to Biochar and *Delonix regia* treated and untreated soils for DGT measurement

Amount of MQ water (mls)/100g soil			
Soil	Control	Biochar	*Delonix regia*
Ijero	36	39	39
Ilesha	40	40	42
Ife	46	44	45
Ekiti OM	22 / 72g soil	24	23/72
Ilesha OM	20/72	21	22/72
Ekiti pH 4	38	40	42

The well mixed soils were left to equilibrate for 24 hours before they were divided into three clean pots. The DGT devices which have been smeared with some of the soil sample were gently pushed into the surface of the soil slurry ensuring that the filter on the window had good contact with the soil. The whole set up were placed in containers where it could be covered with foil paper to prevent loss of water due to evaporation. Deployment were carried out on day 5, day 21 and day 42 of the soil aging; each deployment was done for 24 hours taking note of the average temperature during the deployment period. At the end of the deployment time, the devices were retrieved from the soils and rinsed with MQ water to remove any soil particles from its surface. The devices were opened and with the aid of tweezers the Chelex binding layers were removed and transferred into clean 1.5ml centrifuge tubes. 1ml of 1M HNO_3 was pipetted into the centrifuge tubes for the elution of metals from the binding gels, elution was done for a minimum period of 24 hours after which the samples were diluted and analysed with the ICP-MS.

6.2.2.8 Soil solutions

Immediately after the retrieval of the binding layers from each of the deployed DGT devices, the remaining soils were transferred into 50ml centrifuge tubes and centrifuged at 3000 revolution per minute for 10 minutes in order to complete the soil solutions extraction process. A 1ml aliquot was taken from these and centrifuged further at 6000 rpm for 5minutes. Dilution was done with 0.1M HNO_3 before ICP-MS analysis.

6.2.2.9 Calculation of DGT measured concentration, C_{DGT}

The DGT measurement gives the time-integrated concentrations of pollutants over the period of deployment. From the concentration (C_e) obtained after analysing the elution sample with ICP-MS, mass (M) can be calculated from equation 6.1.

$$M = {C_e(V_{acid} + V_{gel})}/{fe} \quad \text{.....Equation 6-1}$$

Where *fe* is an elution factor of 0.8 (80% of the analyte bound to the binding layer is eluted), V_{acid} is the volume of 1M HNO_3 used in eluting the metal from the resin gel, V_{gel} is the volume of the gel. The DGT measured time-integrated interfacial concentration, C_{DGT}, can be calculated from equation 6.2

$$C_{DGT} = \frac{M\Delta g}{DAt} \quad \text{.....Equation 6-2}$$

Where g is the diffusive layer thickness (filter paper and diffusive gel), D is the diffusion coefficient, t is the deployment time and A is the area of the device exposed to the soil solution (Davlson and Zhang, 1994).

6.2.2.10 Calculation of Index of resupply, R value

The ratio of DGT-measured analyte concentrations (C_{DGT}) to the independently measured soil solution concentration (C_{soln}) referred to as R value, represented in equation 6.3 is an indication of the ability of the solid phase to resupply the analyte to soil solution, it has values between 0 to 1.

$$R = \frac{C_{DGT}}{C_{soln}}$$ .....Equation 6-3

R value close to 1 implies a very rapid resupply of the analyte from soil particles to soil solution but when the R value is less than 0.1, it indicates very little resupply of the analyte (Harper et al., 2000). The R value is used as a measure of the depletion of soil solution concentration at the DGT-medium interface (Ernstberger et al., 2002, Zhang et al., 2006).

6.2.2.11 Calculation of the Distribution Coefficient K_d

The distribution coefficient K_d as estimated in equation 6.4 is the ratio of the concentration of the labile analyte associated with the solid phase to the concentration in soil solution (Lehto et al., 2008). It represents a labile pool size, the adsorbed species that can be available for DGT measurement (Di Bonito et al., 2008, Harper et al., 2000).

$$K_d = \frac{C_{solid\ phase}}{C_{soil\ solution}}$$ .....Equation 6-4

When Kd value is high, it means that the metal specie has been retained by the solid phase through adsorption, whereas when it is low, it implies that high amount of the metal specie is occurring in soil solution.

6.2.2.12 Introduction to DIFS model

A numerical model, DGT-Induced Flux in Sediments and soils (DIFS) was developed to interpret further the DGT measurements and to obtain labile pool size and kinetic information of exchange processes (Harper et al., 1998).

It makes use of the distribution coefficient (Kd) and R value to determine or estimate the response time of the system to perturbation (Tc), and the dissociation rate constant (k_{-1}). (Harper et al., 2000, Harper et al., 1998).

The response time Tc can be expressed as the inverse of the dissociation rate constants showed in equation 6.5 (Harper et al., 2000).

$Tc = \frac{1}{k_1 + k_{-1}}$…… Equation 6-5

It can be obtained from the DFIS model if R and Kd are known. The relationship between R, Kd and Tc can be quantified by the DIFS model if the input parameters of particle concentration (Pc), soil porosity (Φ), and the diffusion coefficients of the metals in the soil (Ds) shown in equations 6.6 to 6.8 are supplied (Boulding, 1996, Harper et al., 1998).

$Pc = \frac{m}{V}$……Equation 6-6

$\Phi = \frac{dp}{(Pc + dp)}$……. Equation 6-7

$Ds = {Do}/{(1 - ln(\Phi^2))}$……..Equation 6-8

With m being the total mass of soil particles; V is the porewater volume in a given volume of total soil; Do is the diffusion coefficient in water and dp is the density of the soil.

The dissociation rate constant k_{-1} is estimated by using the equation 6.9 (Harper et al., 2000)

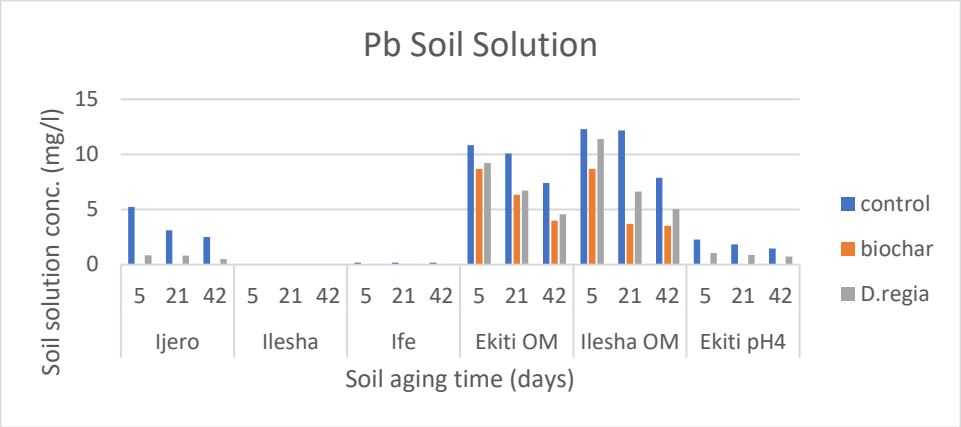
$$k_{-1} = {}^{1}/_{((1+K_d P_c)T_c)} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\text{Equation 6-9}$$

6.3 Results and Discussion

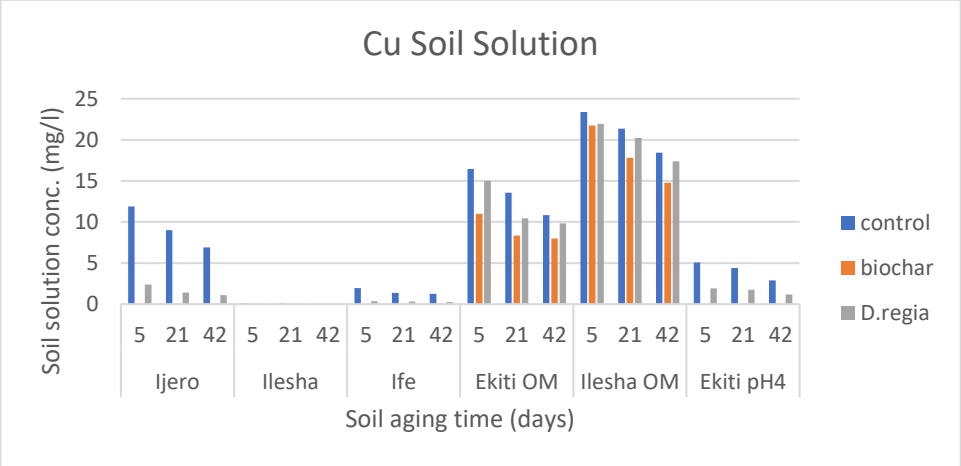
6.3.1 *Metal concentration available in Soil Solutions*

Plants obtain nutrients and also invariably take up whatever ions (including heavy metals) that dissolved from the solid phase to the soil solution (Rieuwerts et al., 1998, Violante et al., 2010). In order to assess the available metal concentration present in soil solution, the steps listed in section 6.2.2.8 were carried out and the results are presented in Figure 6.1a-c.

(a)



(b)



(c)

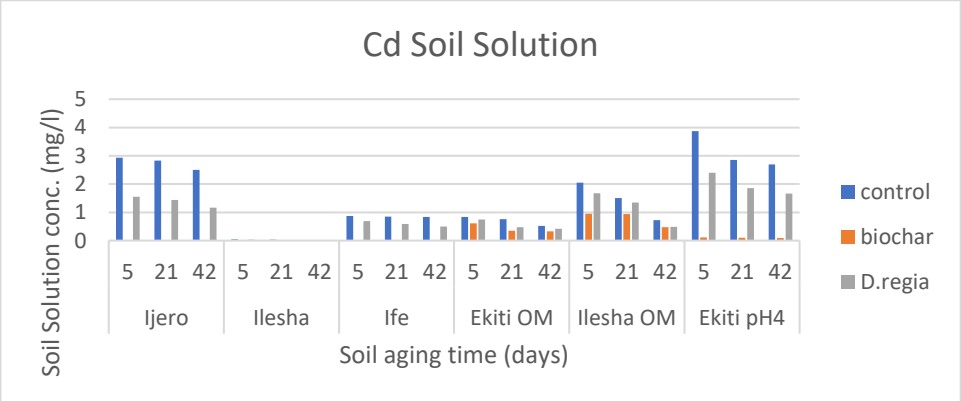


Figure 6-1 (a-c): Determination of total dissolved concentrations of Cu, Cd and Pb in soil solutions of some soils treated and untreated with 2% (w/w) Biochar and 2% (w/w) *Delonix regia*.

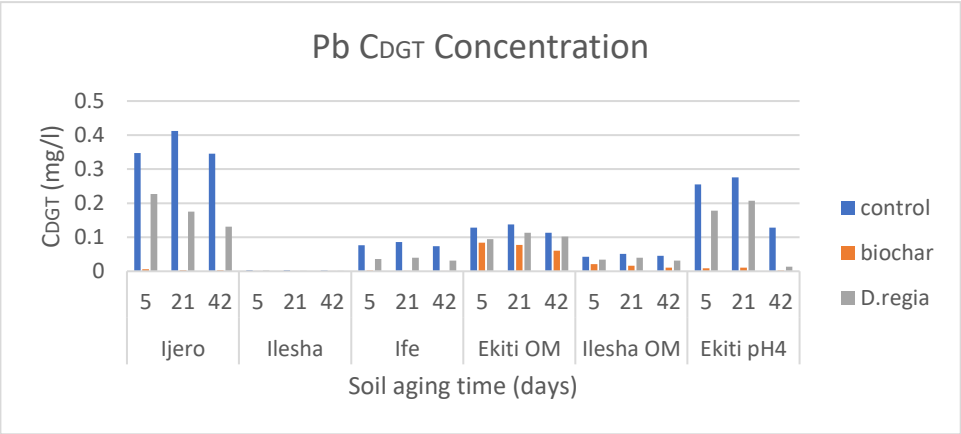
From this figure, all the control soils have the highest soil solution concentration of individual metal (Pb, Cu and Cd). In the biochar treated soils, no observable concentration of these metals was determined in the soil solution samples, except in the soils that were amended with humic acid particles. Similar report that OM makes copper available in form accessible to plants was given by Arán et al. (2016). The values obtained for cadmium in most soils were below the detection limit of the ICP-MS (X Series II) but there was an increase in the Cd soil solution concentration in biochar treated sample of Ekiti pH 4 soil as Cd can transform from the immobile form (carbonates or iron or manganese oxide bound form) to an easily available or exchangeable form at low pH (Li et al., 2014a, Xian and Shokohifard, 1989).

The presence of organic particles (humic particles) in the soils increased the soil solution concentration of all studied metals, notwithstanding the treatment and soil type. Some studies have shown that biochar rich in dissolve organic carbon are able to increase copper mobility in soil (Beesley et al., 2010, Park et al., 2011). The use of *D.regia* also resulted in a reduction in Css for all metals; although the Css for *D.regia* treated soil samples were higher than the biochar treated soils because the ability of different solid phases for retention of ions differs (Martínez and McBride, 1999). Cadmium Css was highest in soil at low pH, Gramlich et al. (2018) reported high Cd availability in alluvial soil with low pH. The marked difference in Css between Ijero and Ife soils (with similar soil pH and organic matter but different CEC) might be as a result of the CEC difference.

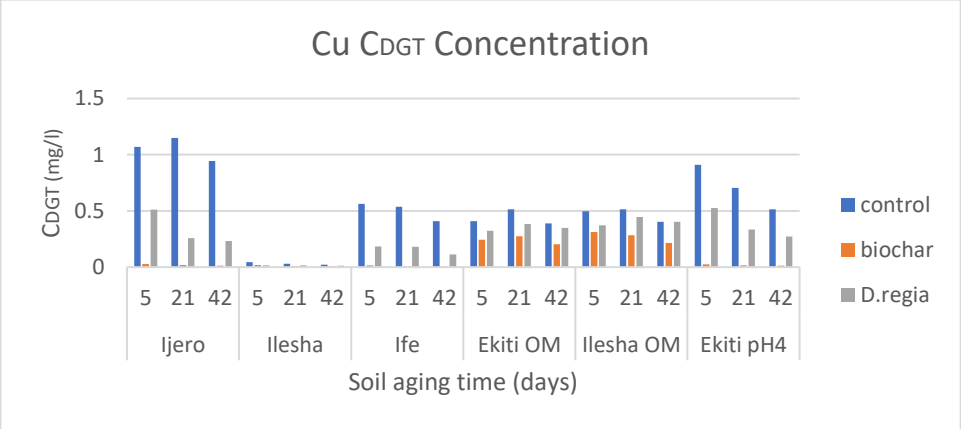
6.3.2 *DGT measured labile concentration (C_{DGT})*

The DGT measurement, C_{DGT}, gives the time-integrated labile concentrations of pollutants over the period of deployment. The result obtained are shown in Figure 6.2 below:

(a)



(b)



(c)

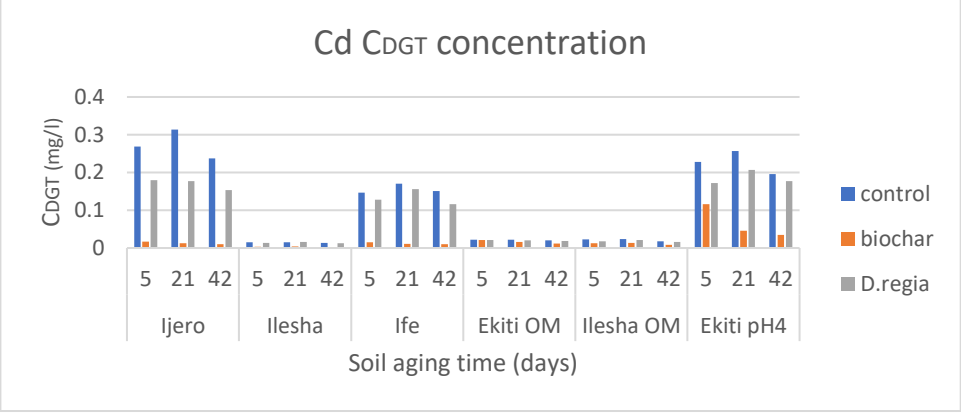


Figure 6-2 (a-c): Determination of C_{DGT}-labile Cu, Cd and Pb in some soils remediated with 2% (w/w) Biochar and 2% (w/w) *Delonix regia* with 42 days incubation period.

The concentration of metals measured by the DGT devices (C_{DGT}) were highest in all control soil samples. On biochar treated soils the C_{DGT} were extremely low (below detection limit of machine in some samples). In Ekiti soil with humic particles, C_{DGT} of lead on biochar remediated soil presented in Figure 6.2(a) was higher than in its counterpart (Ijero) soil without humic particles while for control and *Delonix regia* treated soils, the opposite was evident. Generally, lead C_{DGT} in biochar treated soils were the lowest, *D.regia* treated soils have intermediate C_{DGT} between the control and the biochar treated soils.

Ijero soil was observed to have higher C_{DGT} of copper than Ife soil. The addition of organic matter to Ilesha and Ekiti soils led to an increase in copper C_{DGT} in soils with biochar amendment but the presence of organic matter caused a decrease in copper C_{DGT} in control and *D.regia* treated soils. Uchimiya et al. (2010) reported that when organic matters have high carboxyl functional groups, they can mobilize copper retained by alkaline soils. This might be responsible for the increase copper C_{DGT} in these OM rich soils when treated with biochar.

Experimental error might be the reason for the result obtained for the Cadmium C_{DGT} measured in Ilesha soil (with organic matter) which was higher than in corresponding soils without added organic matter.

Ekiti OM soils (soils with similar properties with Ijero except in CEC values), have lower Cd C_{DGT} than Ijero soils without added organic matter; it might be because of the higher CEC in Ekiti soil and the sorptive ability of humic particles for metals (Cambier et al., 2014).

6.3.3 *The index of resupply, R*

The ratio of DGT-measured analyte concentrations (C_{DGT}) to the independently measured soil solution concentration (C_{soln}) referred to as R value (Equation 6.10) is an indication of the ability of the solid phase to resupply the analyte to soil solution. The closer the value of the resupply index, R to unity, the rapid the resupply of the metal from the solid phase to solution, Tables 6.2 to 6.5 represented the obtained R values for the study.

$R = \frac{C_{DGT}}{C_{soln}}$…….. Equation 6-10

Across all the soils, the average resupply of lead from the solid phase to soil solution is highest in the control soil of most samples (except in Ijero). The control samples were able to resupply each of the metals studied moderately back to soil solution. R values obtained for the resupply of metals in the treated samples did not follow a regular pattern, in Ijero soil for instance, the resupply of lead in biochar treated soil was higher than *D.regia* treated soil but in Ilesha soil, the opposite was observed in the treated soils.

Table 6-2: R values for Ijero soil with and without biochar and *Delonix regia* treatment

		Cu (R) value			Cd (R) value			Pb (R) value		
Soil	Day	Con	Bio	De	Con	Bio	De	Con	Bio	De
Ijero	5	0.09	0.80	0.22	0.09	BDL	0.12	0.07	0.66	0.27
	21	0.13	0.58	0.18	0.12	BDL	0.12	0.13	0.39	0.21
	42	0.14	BDL	0.21	0.1	BDL	0.12	0.14	0.83	0.26
	Average	**0.12**	**0.69**	**0.21**	**0.10**	**BDL**	**0.12**	**0.11**	**0.63**	**0.25**

Table 6-3: R values for Ilesha soil with and without biochar and *Delonix regia* treatment

		Cu (R) value			Cd (R) value			Pb (R) value		
Soil	Day	Con	Bio	De	Con	Bio	De	Con	Bio	De
Ilesha	5	0.50	0.58	0.35	0.32	BDL	0.36	0.33	0.20	0.33
	21	0.41	BDL	0.81	0.52	BDL	0.58	0.47	0.13	0.26
	42	0.99	BDL	0.46	1.09	BDL	0.63	0.42	0.15	0.33
	Average	**0.63**	**0.58**	**0.54**	**0.42**	**BDL**	**0.52**	**0.40**	**0.16**	**0.31**

Table 6-4: R values for Ife soil with and without biochar and *Delonix regia* treatment

		Cu (R) value			Cd (R) value			Pb (R) value		
Soil	Day	Con	Bio	De	Con	Bio	De	Con	Bio	De
Ife	5	0.29	0.86	0.53	0.17	BDL	0.19	0.39	0.16	1.13
	21	0.39	0.76	0.56	0.20	BDL	0.27	0.51	0.08	1.32
	42	0.33	0.81	0.47	0.18	BDL	0.23	0.44	0.16	1.86
	Average	**0.34**	**0.81**	**0.52**	**0.18**	**BDL**	**0.23**	**0.45**	**0.13**	**error**

Table 6-5: R values for Ekiti OM soil with and without biochar and *Delonix regia* treatment

		Cu (R) value			Cd (R) value			Pb (R) value		
Soil	Day	Con	Bio	De	Con	Bio	De	Con	Bio	De
Ekiti	5	0.02	0.02	0.02	0.03	0.03	0.03	0.01	0.01	0.01
OM	21	0.04	0.03	0.04	0.03	0.05	0.04	0.01	0.01	0.01
	42	0.04	0.03	0.04	0.04	0.04	0.04	0.02	0.02	0.02
	Average	**0.03**	**0.03**	**0.03**	**0.03**	**0.04**	**0.04**	**0.01**	**0.01**	**0.01**

Table 6-6: R values for Ilesha OM soil with and without biochar and *Delonix regia* treatment

		Cu (R) value			Cd (R) value			Pb (R) value		
Soil	Day	Con	Bio	De	Con	Bio	De	Con	Bio	De
Ilesha	5	0.02	0.01	0.02	0.01	0.01	0.01	0.003	0.002	0.003
OM	21	0.03	0.02	0.02	0.02	0.01	0.02	0.004	0.004	0.006
	42	0.02	0.02	0.02	0.03	0.02	0.03	0.006	0.003	0.007
	Average	**0.02**	**0.02**	**0.02**	**0.02**	**0.01**	**0.02**	**0.004**	**0.003**	**0.005**

Table 6-7: R values for Ekiti pH$_4$ soil with and without biochar and *Delonix regia* treatment

		Cu (R) value			Cd (R) value			Pb (R) value		
Soils	Day	Con	Bio	De	Con	Bio	De	Con	Bio	De
Ekiti	5	0.18	0.72	0.28	0.06	0.35	0.07	0.11	1.47	0.17
pH 4	21	0.16	0.68	0.19	0.09	0.46	0.11	0.15	4.39	0.24
	42	0.18	0.64	0.23	0.07	0.4	0.11	0.09	1.87	0.02
	Average	**0.17**	**0.68**	**0.23**	**0.07**	**0.40**	**0.10**	**0.12**	**error**	**0.14**

The resupply of copper from soil solid phase was highest (between 0.56 and 0.80) in the biochar treated soils, followed by *D.regia* and the soil with the lowest resupply (0.18 and 0.40) was the control soil. This indicate that the buffering capacity of the biochar treated soils for the copper is high and copper in the solid phase could be resupplied to the solution fastest in bio-treated soils than those with *D.regia* treatment or control soils where the soil buffering capacity is poor.

Cd soil solution concentrations were below the detection limit and so its resupply in these soils could not be estimated.

The resupply of cadmium in *D.regia* treated soils (between 0.16 and 0.60) were greater than in all the corresponding control soils (between 0.06 and 0.52). It can be concluded from the result that the index of metal resupply is generally higher in all biochar amended soils except in OM soils.

In all the soils to which organic matter were added, resupply of metal was very low as seen in the relatively low R values (0.02 and 0.03). The resupply of Pb, Cu and Cd from solid phase to solution was very low in all organic matter amended soils, this might be due to the conversion of organic complexes into stable form for binding metals (Martínez and McBride, 1999).

6.3.4 Labile pool size of K_d values

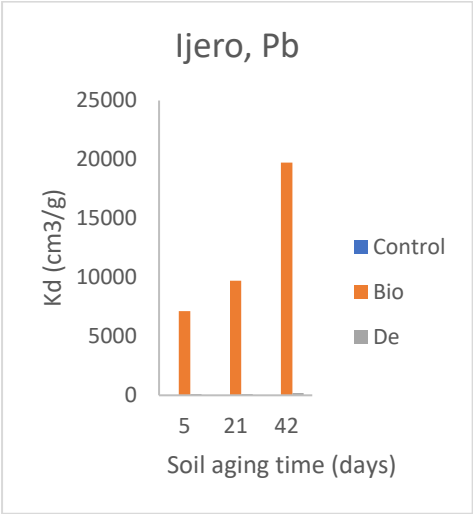
The distribution coefficient Kd shown in equation 6.11 is a ratio used to express the relation between the concentration of the labile metal associated with the solid phase to the concentration in soil solution (Lehto et al., 2008). It is an indication of the labile pool size of the metal that can be available for DGT measurement (Di Bonito et al., 2008, Harper et al., 2000).

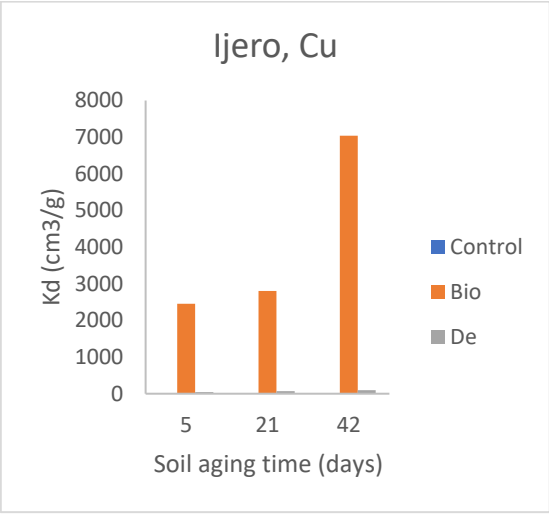
$$Kd = \frac{C_{solid\ phase}}{C_{soil\ solution}} \quad \text{.....Equation 6-11}$$

The $C_{solid\ phase}$ is the concentration of each metal obtained by extraction with 0.01M $CaCl_2$ while the $C_{soil\ solution}$ is the concentration of the metal in soil solution obtained by centrifugation. Methods for the extraction and soil solution are in section 5.2.2.5 and 6.2.2.8 respectively.

The DIFS model was applied to the obtained (R) values (Tables 6.2 to 6.7) in order to determine Kd values and Tc; it is assumed that the Kd calculated by $CaCl_2$ extraction is close to labile Kd that can be obtained by DFIS.

The results obtained for the coefficient of distribution of the labile pool, Kd values for Cu, Cd and Pb in this study are presented in Figure 6.3.


Ijero, Pb
25000
20000
15000
10000
5000
0
Kd (cm3/g)
5
21
42
Soil aging time (days)
Control
Bio
De


Ijero, Cu
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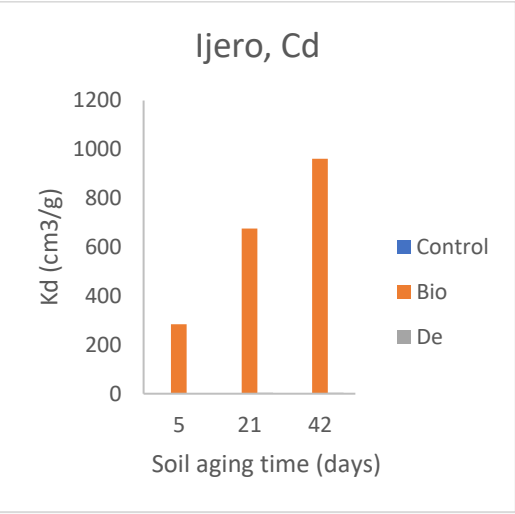
7000
6000
5000
4000
3000
2000
1000
0
Kd (cm3/g)
5
21
42
Soil aging time (days)
Control
Bio
De


Ijero, Cd
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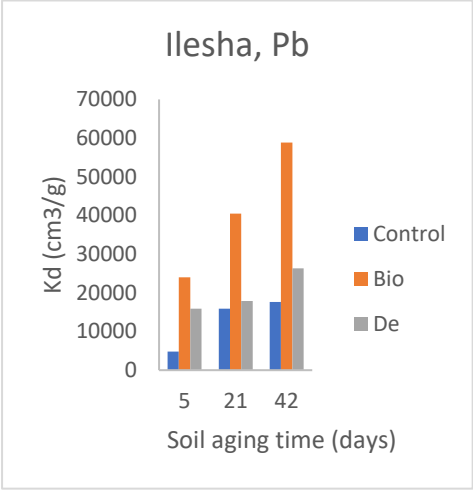
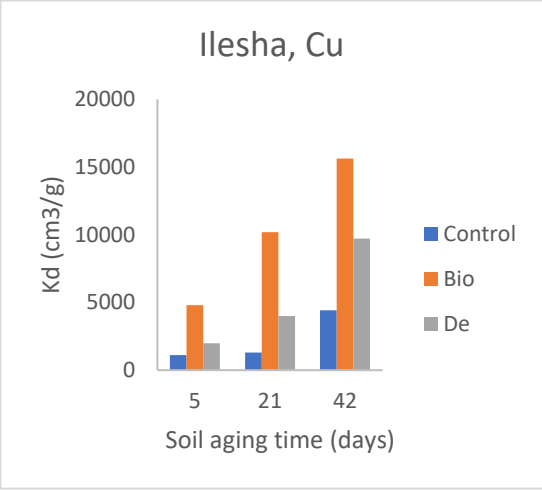
1000
800
600
400
200
0
Kd (cm3/g)
5
21
42
Soil aging time (days)
Control
Bio
De


Ilesha, Pb
70000
60000
50000
40000
30000
20000
10000
0
Kd (cm3/g)
5
21
42
Soil aging time (days)
Control
Bio
De


Ilesha, Cu
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10000
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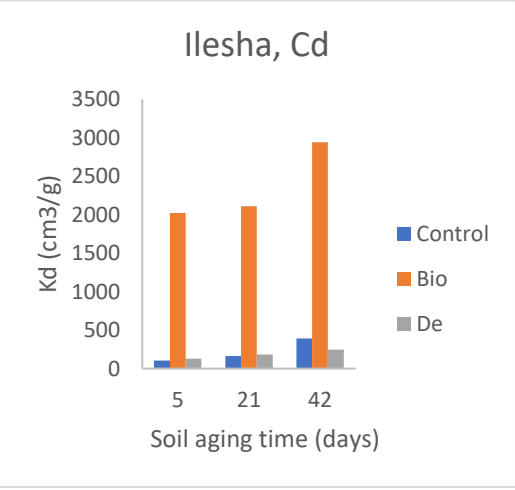
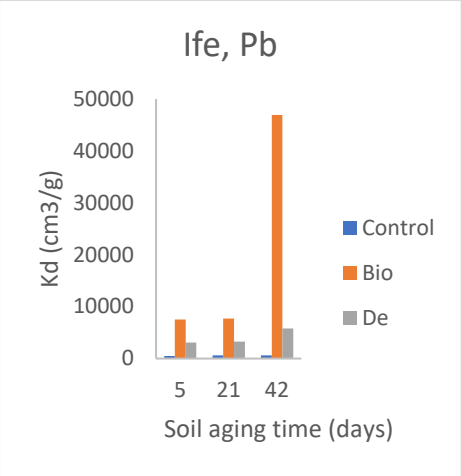
Kd (cm3/g)
5
21
42
Soil aging time (days)
Control
Bio
De


Ilesha, Cd
3500
3000
2500
2000
1500
1000
500
0
Kd (cm3/g)
5
21
42
Soil aging time (days)
Control
Bio
De


Ife, Pb
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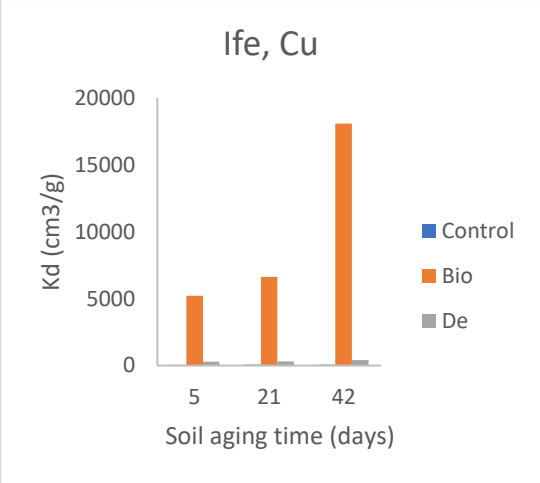
30000
20000
10000
0
Kd (cm3/g)
5
21
42
Soil aging time (days)
Control
Bio
De


Ife, Cu
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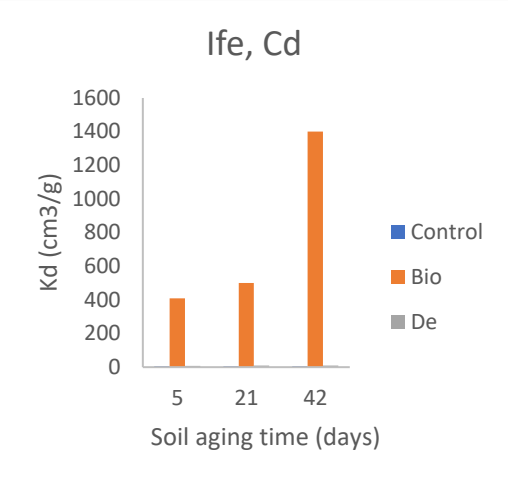
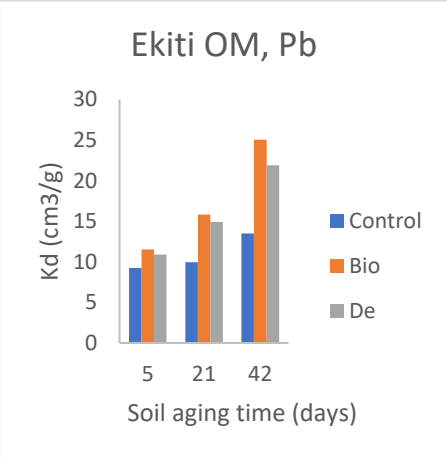
15000
10000
5000
0
Kd (cm3/g)
5
21
42
Soil aging time (days)
Control
Bio
De


Ife, Cd
1600
1400
1200
1000
800
600
400
200
0
Kd (cm3/g)
5
21
42
Soil aging time (days)
Control
Bio
De


Ekiti OM, Pb
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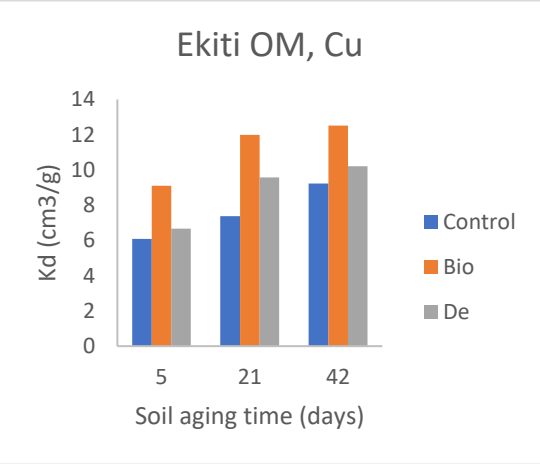
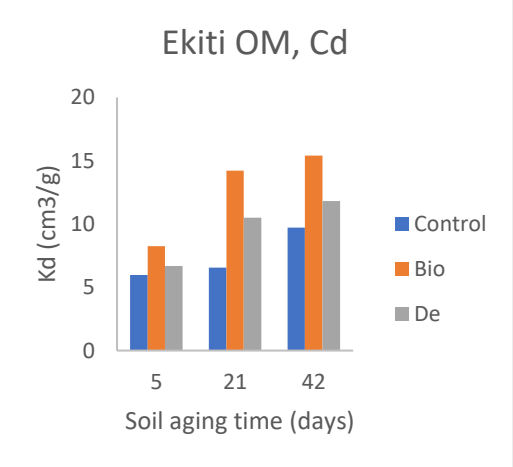
25
20
15
10
5
0
Kd (cm3/g)
5
21
42
Soil aging time (days)
Control
Bio
De


Ekiti OM, Cu
14
12
10
8
6
4
2
0
Kd (cm3/g)
5
21
42
Soil aging time (days)
Control
Bio
De


Ekiti OM, Cd
20
15
10
5
0
Kd (cm3/g)
5
21
42
Soil aging time (days)
Control
Bio
De

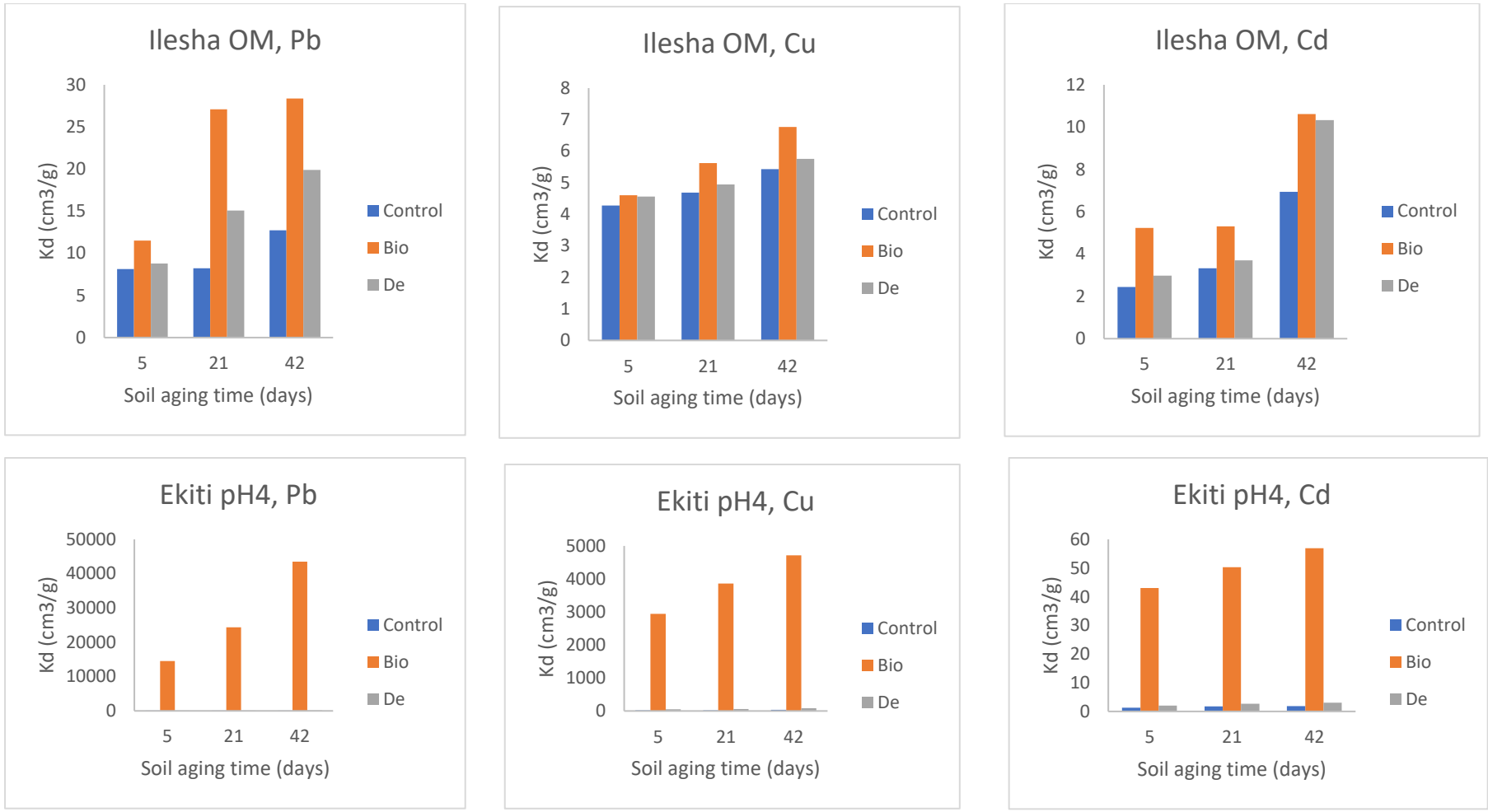


Figure 6-3: Kd values for Cu, Cd and Pb selected soils with and without Biochar and *Delonix regia* treatment.

When Kd value is high, it means that the metal species has been retained by the solid phase through adsorption. Whereas when it is low, it implies that high amount of the metal species are partitioning into soil solution.

Biochar treated soils have the highest Kd values in all the soil types irrespective of metals. The Kd values obtained from biochar treated soils for each metal was (Pb was at least 700 times more; Cu was at least 2400 times more; Cd was at least 200 times more) than the Kd in the *Delonix regia* treated and the control samples.

This means that a large proportion of metals in the biochar treated soils are in the soil solid phase and can be redistributed to soil solution. In all the soils, Kd for the metals in the *D.regia* treated soil was next in value to the biochar treated soil while the control soil sample had the least value. Thus the labile pool size of metals (Pb, Cu and Cd) that can be resupplied to soil solution from the soil solid phase in this work follows this order: Bio-treated soils > *D.regia* treated soils > control soil samples. In soils amended with humic particles, a considerable labile pool size was obtained for the studied metals; Lead labile pool size was found to be the largest followed by cadmium and lastly copper. Across all soils samples Kd values for lead was the highest while the lowest value was obtained by cadmium. Although the spiked concentration of cadmium was the least at the onset of the study, but this observation might be because lead is able to form many complexes with ligands on the humic acid functional groups and thus be made resident in the solid phase more than cadmium.

6.3.5 *Response time (Tc) and resupply rate constant (k_{-1})*

The response time to depletion for the system; Tc is an indication of the time needed for the disequilibria of labile metals induced by DGT to revert to 63% of the equilibrium value (Guan et al., 2017). From Table 6.8, the result for lead Tc in the

control samples of (Ijero and Ekiti pH 4) and biochar treated samples of (Ilesha and Ife) have the highest value. Tc value of 23600s in Ijero control sample and 9505s in Ilesha biochar treated soil. It is observed that soil with high and moderate CEC (Ilesha and Ife) have highest response times when biochar treatment is used while those soils with low CEC (Ijero) have the highest Tc in control samples. When humic particles were added to Ekiti and Ilesha soils, response time of higher magnitude (10^7s) were observed and this value remained the same for the control samples, biochar- and *Delonix regia*-treated soils. The values of response time for all studied metals in majority of *D.regia* treated soils were generally between the values obtained for control and biochar amended soils.

The average Tc for copper and cadmium in biochar amended soil were the lowest (copper has Tc of 200s while cadmium has 0.001s on Ijero soil). From these results, the rate at which biochar treated soil is able to resupply the metals bound to its solid phase is very fast. The control soil samples have high Tc values (6330s for copper on Ijero and 4176s for cadmium on the same soil) which means it will take longer time before metals can be resupplied from its solid phase to solution. Tc in *Delonix regia* treated soil is intermediate between control samples and biochar treated soil samples. Although biochar treated soils have large coefficient of distribution for each of the metals, but it also has the fastest resupply, thus, from the kinetic point of view remediation of heavy metal contaminated soils with biochar will be considered ineffective. The response time of *Delonix regia* treated soils is faster than those obtained for the control soils; and it might not be a good choice for remediation as well.

The result also showed the trend below for the response time of each metals in the soils:

Pb Tc: Ife<Ijero<Ilesha<Ekiti Ph4<Ilesha OM=Ekiti OM soils;

Cu Tc: Ekiti Ph4<Ijero<Ife<Ilesha<Ilesha OM=Ekiti OM soils;

Cd Tc: Ife<Ijero<Ekiti Ph4<Ilesha OM=Ekiti OM. Cd in Ilesha soil is below detection limit.

From the trend, it could be said that the response time in organic matter rich soils is very low for all metals and in all soil samples since humic particles could act as adsorbent and increase the binding and sorption ability of the soils. Ilesha soil has the next slower response time probably because it has higher CEC value than other soils; it means it has higher sorption or ability to hold metal to itself than soils with lower CEC. Ife, Ijero and Ekiti pH 4 soils have the fastest response time depending on the metal considered, may be because these soils have low or moderate CEC, low pH, and poor organic matter content (humic acid was not added to them) and (the low clay content in Ijero soil); these properties must have contributed to the fast response time in these soils. Low pH enhances metal mobility in soil (Ekiti pH 4 soil); Low CEC and low clay content reduces the sorptive ability of soil for metals (Ijero and Ife soils).

Ijero and Ekiti soils were collected in the same region and the soils have similar properties except for the difference in CEC.

Table 6-8: Response time, Tc, (s) values obtained for Cu, Cd and Pb in selected soils with and without Biochar and *Delonix regia* treatment

	Ijero			Ekit with OM		
			Day 5			
	Cu	Cd	Pb	Cu	Cd	Pb
Control	$1.38*10^4$	0.40	$2.36*10^4$	$1.0*10^7$	$1.0*10^7$	$1.00*10^7$
2% Bio	63	BDL	286.8	$1.0*10^7$	$1.0*10^7$	$1.00*10^7$
2% De	1476	$1.45*10^3$	701.5	$1.0*10^7$	$1.0*10^7$	$1.00*10^7$
			Day 21			
Control	6330	0.001	5046	$9.44*10^5$	$1.0*10^7$	$1.00*10^7$
2% Bio	199.9	BDL	589.7	$1.0*10^7$	$1.90*10^5$	$1.00*10^7$
2% De	3182	3649	$1.69*10^3$	$1.0*10^7$	$2.76*10^5$	$1.00*10^7$
			Day 42			
Control	6023	4176	4220	$3.11*10^6$	$3.69*10^5$	$1.00*10^7$
2% Bio	BDL	BDL	86.07	$1.0*10^7$	$1.0*10^7$	$1.00*10^7$
2% De	1965	2885	$9.98*10^2$	$1.0*10^7$	$1.98*10^5$	$1.00*10^7$
	Ife			**Ekiti @ pH4**		
			Day 5			
Control	701.9	1.52	345	1852	$3.32*10^4$	6439
2% Bio	30.03	BDL	5401	53.91	32.15	BDL
2% De	124.1	230.6	0.02	732.4	$2.38*10^4$	2981
			Day 21			
Control	289.4	326.6	184.8	4378	$1.04*10^4$	4270
2% Bio	589.5	BDL	$3.34*10^4$	91.11	0.04	BDL
2% De	149.6	2.67	0.03	3039	4999	1367

			Day 42			
Control	651.2	158.2	291.3	2810	$2.68*10^{4}$	$1.59*10^{4}$
2% Bio	31.3	BDL	6978	96.98	96.79	18.56
2% De	283.1	0.02	BDL	1773	6397	$1.0*10^{7}$
	Ilesha			**Ilesha with OM**		
			Day 5			
Control	210	$6.24*10^{2}$	4318	$5.03*10^{2}$	$1.0*10^{7}$	$1.00*10^{7}$
2% Bio	133.1	BDL	2037	$1.51*10^{-1}$	$1.0*10^{7}$	$1.00*10^{7}$
2% De	628.1	470.3	626.2	$1.66*10^{-1}$	$1.0*10^{7}$	$1.00*10^{7}$
			Day 21			
Control	450.4	$1.32*10^{2}$	285.3	$1.0*10^{7}$	$1.0*10^{7}$	$1.00*10^{7}$
2% Bio	BDL	BDL	9505	$1.0*10^{7}$	$1.0*10^{7}$	$1.00*10^{7}$
2% De	111.7	0.043	2212	$1.0*10^{7}$	$6.23*10^{2}$	$1.00*10^{7}$
			Day 42			
Control	BDL	BDL	283.3	$1.0*10^{7}$	$1.0*10^{7}$	$1.00*10^{7}$
2% Bio	BDL	DBL	4930	$1.0*10^{7}$	$1.0*10^{7}$	$1.00*10^{7}$
2% De	BDL	52.84	1043	$1.0*10^{7}$	$1.0*10^{7}$	$1.00*10^{7}$

The desorption or resupply rate constant k_{-1} was calculated from Tc, Pc and Kd using Equation 6.9. The values obtained for all studied soils samples (before and after remediation with 2% biochar and 2% *Delonix regia*) are shown in Table 6.9. Generally, the highest values of Tc produce minimum values of k_{-1}. The desorption

rate constant for lead in the Ijero remediated soils showed that biochar treated soils have the least values except in Ijero and Ekiti pH 4 soils.

Table 6-9: Dissociation rate constant, k_{-1} estimated for Pb, Cu and Cd on control and soil samples remediated with 2% (w/w) Biochar and 2% (w/w) *Delonix regia*

Metal/soil	Pb	Cu	Cd
k_{-1} value in Ijero soil			
Control	1.7e-07	3.40e-06	5.33e+01
Biochar	1.63e-07	1.85e01	2.74e-02
Delonix regia	2.85e-06	3.37e-06	4.37e-05
k_{-1} value in Ilesha soil			
Control	6.29e-08	2.81e-01	8.55e-03
Biochar	3.54e-09	2.16e-01	9.27e-01
Delonix regia	2.27e-08	1.44e-01	1.76e-02
k_{-1} value in Ife soil			
Control	3.35e-06	1.44e-05	1.64e-02
Biochar	4.63e-09	1.23e-06	2.77e-02
Delonix regia	2.41e+00	8.83e-06	9.51e-01
k_{-1} value in Ekiti OM			
Control	2.8e-09	1.91e-08	3.07e-08
Biochar	2.06e-09	2.94e-09	4.21e-08
Delonix regia	2.13e-09	3.61e-09	8.15e-08
k_{-1} value in Ilesha OM			
Control	1.81e-09	4.04e-05	7.25e-09
Biochar	1.52e-09	1.32e-01	4.39e-09
Delonix regia	2.29e-09	1.26e-01	4.08e-05
k_{-1} value in Ekiti pH 4			
Control	1.1e-06	5.96e-06	1.01e-05
Biochar	1.46e-01	1.51e-06	6.36e-02
Delonix regia	2.06e-06	5.33e-06	1.77e-05

Soil with highest k_{-1} is quick to release metal bound to it and the one with lowest k_{-1} signifies the stronger the material retains the metal, and therefore the slower the desorption will occur.

The desorption rate constants for lead were highest in the control samples of Ilesha and Ekiti OM while *D.regia* had highest k_{-1} values in Ijero, Ife and Ilesha OM soils, biochar had highest k_{-1} value in Ekiti pH 4 soil. For Copper: control samples had

highest in Ilesha, Ife, Ekiti OM, and Ekiti pH 4 soils while biochar recorded the highest k_{-1} in Ijero and Ilesha OM soils.

In the case of cadmium, *Delonix regia* had highest value on Ife, Ekiti OM and Ilesha OM soils while Ilesha and Ekiti pH 4 soil have highest k_{-1} for Cd in biochar treated soils. The only soil with highest Cd k_{-1} in control sample is the Ijero soil.

Generally, the desorption rate constants for lead and copper before remediation were higher than those calculated from at least one of the treated soil samples but for cadmium, the desorption rate constant was in most soils the lowest before remediation was carried out.

Lead k_{-1} was higher in biochar treated soils than in *D.regia* treated soils in all soil samples used in this study except Ekiti pH 4 indicating that the desorption of lead from biochar treated soils is slower than in the *D.regia* treated soils; making biochar treatment more effective than *D.regia* material for lead removal. The Pb k_{-1} obtained for *D.regia* treatment appeared to the highest.

The un-remediated soils (except Ijero and Ilesha OM) have the highest k_{-1} for copper. The effectiveness of remediation treatment based on the values of k_{-1} cannot be predicted precisely because the trend obtained for both treatment types were fluctuating, although *D.regia* treatment seemed more effective in most of the soils. The desorption of copper occurs slower in the treated soils than in the un-remediated soils. The desorption rate constant for cadmium is lowest before remediation was carried out on the contaminated soils. Though from this, it means the treatments were not effective for cadmium removal from resupply point of view, but biochar treatment was more effective than *D.regia* treatment.

6.3.6 *Assessing aging effect on R, K_d T_c*

No generalized trend can be drawn out on the effect of aging on R values for the studied metals. The pattern observed was fluctuating with increase in aging time. It is only in the organic matter amended soil that the R values remained unchanged for each metal with aging.

The Kd values for all the metals in all soils and treatment types were increasing with the aging time.

Response time, Tc for all the metals decreased with aging in most of the control soil samples. Aging increased the response time for copper and lead on biochar treated soils, but decreased Cd Tc was observed with aging in biochar treated soils. The pattern observed for copper and lead Tc on *D.regia* treated soils were increased Tc with aging, cadmium decreased with aging. Aging had no effect on the Tc of any metal in the OM soils irrespective of the treatment applied.

6.4 Conclusion

This chapter focussed on the assessment of the remediation treatment of contaminated soils by biochar and *D.regia* using the DGT technique and kinetic modelling by 1D-DIFS. It showed generally that each of the treatments have remarkable reducing effects on the available concentration of the studied metals in contaminated soils.

Reduction in Css and C_{DGT} concentrations for treated soil samples is in this order: Bio-treated soils < *D. regia* treated soils< control samples. That is the available metal concentration in both treated soils were reduced compared with the control samples; an evidence of the good remediation that was achieved by each treatment. In organic

rich soil, the presence of humic particles in the soils increased the soil solution concentration of all studied metals, practically, this might mean that remediation of organic matter rich soil will not yield good result. R values obtained for the resupply of metals in the treated samples did not follow a regular pattern.

The labile pool size (Kd) of metals (Pb, Cu and Cd) that can be resupplied to soil solution from the soil solid phase is in this order: Bio-treated soils > *D.regia* treated soils > Control soil samples. In soils amended with humic particles, very small labile pool size was obtained for the studied metals. Lead labile pool size was found to be the largest followed by cadmium and lastly is copper.

The response time (Tc) values followed the order: Control samples > *D.regia* treated soil > biochar treated soils. This depict that the resupply of available metal concentration back into the soil solution will be fastest in the biochar treated soils and slowest in the control soil. From this, it could be concluded that the contaminated soils are better left un-remediated if treated soils will release available metal at a rate that is faster than in untreated soils; this might likely be linked to the source of the soil. In majority of the soils, the trend in magnitude obtained for the Tc values are the same obtained for the desorption rate constant, k_{-1}, a further confirmation that the control soils release available metal to soil solution much slower than the treated soils.

The values obtained for k-1 showed that biochar treatment is effective for lead removal, both treatment types (biochar and *D.regia*) are effective for copper while none of the two treatments used in this work is effective for the removal of cadmium.

Aging effect on the Kd values for all the metals in all soils and treatment types were increasing with the aging time. That means that the labile pool size available for resupplying metals to soil solution is increasing with aging time. In the biochar and

Delonix regia treated soils, Tc increased with aging and *D.regia* have the higher value.

In the OM soils, Tc values were the same for each metal throughout the incubation period. The resupply rate in the control soils were reducing with aging but in the treated soils, it was increasing. It means that bonded metal fractions are released from the soil. The resupply is slower in *D.regia* treated soils than biochar treated soils. The resupply of lead is the faster, than cadmium and the slowest was copper.

Chapter 7. Conclusion and Recommendations

7.1 General Conclusions

The systematic investigation carried out in this study has provided detailed information on the adsorption characteristics of *Delonix regia*, for heavy metals in solution with elevated concentrations, the potential of using *Delonix regia* for remediation of contaminated soils and the assessment of available metals in soils using DGT technique. The work on investigating adsorption characteristics revealed that adsorption of metals onto *Delonix regia* is pH-dependent and the optimum pH for maximum adsorption unto *Delonix regia* pods powder is 4,5,4,6 and 4 for lead, nickel, copper, cadmium and cobalt, respectively, while for the leaves an optimum pH of 5 was recorded for all the metals. The optimum contact time was thirty minutes. Kinetic modelling for lead, nickel, copper, cadmium and cobalt showed that second order kinetic model is applicable. The study also showed that the adsorption is dependent on the initial metal concentration with Langmuir and Freundlich Isotherms being the applicable isotherms for the sorption processes in *D.regia* pods while Freundlich is the only applicable isotherm for sorption of the metals unto the leaves. The maximum capacity of *Delonix regia* pod powder is 31.2mgPb/g; 5.9mgNi/g; 9.1mgCu/g; 6.5mgCd/g and 5.8mgCo/g while the leaves powder has 10.3mgPb/g; 10.3mgNi/g; 9.2mgCu/g; 8.4mgCd/g and 10.3mgCo/g.

The results of these two chapters suggest that *Delonix regia* pods and leaves powder could be used as adsorbent to remove heavy metal from low pH waste stream within a very short time of 30 minutes. The pods powder has high capacity for lead; both the leaves and the pod powder could be used to remove copper; while cobalt, nickel and cadmium removal are better with the leave powder. Moderate uptake of 60% in 0.05M

ionic strength solution showed that the adsorbents could be used effectively in water with lower ionic strength.

When using *Delonix regia* and biochar to remove metals from contaminated soils, the removal efficiency of both type of treatment increased with aging of the contamination. Although both materials could be used on soils contaminated with these metals, biochar is more effective than *Delonix regia*.

The initial concentration of metals had no effect on the removal efficiency of biochar treated soils and thus, biochar would be suitable to use in both low and highly metal contaminated soils but *Delonix regia* will perform better in soils contaminated with low level of contaminants.

Soil pH affected the removal efficiency of both treatment types except for cadmium. Biochar has high removal efficiency (> 70%) at pH 3 to 7 investigated in this work and will thus be a good treatment to use on any polluted soil without pH restraint especially in the highly acidic soil contaminated by heavy metal wastes.

The presence of OM enhanced the removal ability of *Delonix regia* for the metals when soil properties such as CEC are too low; the *Delonix regia* material could be useful as treatment in soils rich in organic matter; the opposite was observed in biochar treated soils, increased removal efficiency was recorded in soils without added organic matter. The results indicate that biochar can be useful in removing metals from weathered and exposed soils like some in the mining areas.

The assessment of the remediation effectiveness by biochar and *D.regia* using the DGT technique and DFIS modelling showed that each of the treatment types has remarkable effects on the available concentration of the studied metals in contaminated soils.

Soil solution concentration of metals in the soils has the order of Bio-treated soils < *D. regia* treated soils < control samples. Removal of heavy metals from organic rich soil, required great caution and a good understanding because the presence of organic particles (humic particles) in the soils increased the soil solution concentration of all studied metals, notwithstanding the treatment and soil, practically, this might mean that remediation of organic matter rich soil will not yield good result.

DGT measured labile concentrations of copper, cadmium and lead were higher in all soils without treatment (control samples) than in the corresponding treated soils. Soil properties such as CEC played a crucial role in immobilizing of metals. Soils treated with biochar have the lowest labile concentrations of metals. The same trend in soil solution was observed.

No clear conclusion can be drawn on the assessment of resupply of metals from soil solid phase based on R values. The R values obtained for the biochar treated soils were higher than obtained in the control and *Delonix regia* treated soils; the R in *D.regia* soils were also higher than in the control samples. This means that the resupply of metal is higher in the treated soils than in the control and that the remediated soils are able to resupply the bond metal and make it available over time. This is a serious issue to critically consider in the application of treatment to soils for remediation purposes.

The labile pool size of metals, Kd, (Pb, Cu and Cd) that can be resupplied to soil solution from the soil solid phase follows the order of Bio-treated soils > *D.regia* treated soils > Control soil samples. All biochar treated soils have very large Kd values that is, the metals in biochar treated soils are present and bound in the solid phase and are part of the available pool of metal for subsequent transfer to soil

solution. Kd values for *D.regia* treated soils stand between the values obtained for control and biochar samples. In soils amended with humic particles, small labile pool size was obtained for the studied metals. The labile pool size of lead was found to be the largest followed by cadmium and lastly is copper, but in all other soils lead labile pool size is followed by copper and lastly cadmium. Soil organic matter are able to initiate a release of bound cadmium into soil solution.

The response time, Tc, has an order of Control samples > *D.regia* treated soil > biochar treated soils. This depict that the resupply of available metal concentration into the soil solution will be fastest in the biochar treated soils and slowest in the control soil. It indicates that the remediation by biochar may not be a good choice if treated soils end up creating more harm by releasing available metal at a rate that is faster than in untreated soils. The values obtained for k_{-1} showed that biochar treatment is effective for lead removal, both treatment types (biochar and *D.regia*) are effective for copper while none of the two treatments used in this work is effective for the removal of cadmium.

The labile pool size (Kd) for all the studied metals in all soils and treatment types increased with the aging time; most significantly in the biochar treated soils. The index of resupply (R), in the control soils were reducing with aging but in the treated soils, it was increasing. The resupply was slower in *D.regia* treated soils than biochar treated soils. In the OM soils, treatment types and aging had no effect on metal resupply. The resupply of lead is the faster, then cadmium and the slowest was copper.

7.2 Recommendations for future work

This work focussed on the single metal system but for future work, the binary and possibly multi-metals systems should be investigated and adsorption with *Delonix regia* on industrial effluents should be considered. Effects of different particle sizes should be studied to ascertain the capacity of *Delonix regia* in removing heavy metals when the particle sizes vary. Adsorption experiments using continuous flow in-column systems should be designed as the adsorbent could be a viable option as a bio-filter in industrial effluents treatment.

Means of recovering (either by electro-recovery or bio-hydrometallurgy) the remaining adsorbed metal on the adsorbent after desorption should be carefully investigated before eventual disposal.

Possible cheap modification, to enhance performance, of *D.regia* pods should be considered. Examples include the conversion of pods to biochar to be used for adsorption, rather than using the unmodified form.

Different application rates of treatment for the remediation of contaminated soils should be looked into as this will give a better picture of the efficiency of the applied treatment; also, long-term remediation processes to monitor the resupply of heavy metals and the efficiency of each treatment on the long run should also be considered and investigated.

Evaluation of the effect of biochar on soil pH in a long-term study should be investigated, to give insight into how long the effect of pH in soil can last after biochar application.

In depth study on the effect of organic matter, *Delonix regia* and biochar in soil remediation should be investigated and detailed study should be engaged to ascertain the trend of Index of resupply, R, with aging during soil remediation exercise.

References

ABOYEJI, O. O. 2013. Freshwater pollution in some Nigerian local communities, causes, consequences and probable solutions. *Academic Journal of Interdisciplinary Studies,* 2**,** 111.

ADELEYE, I. & ADEBIYI, A. 2003. Physicochemical and microbiological assessment of Oko-oba--a Nigerian abattoir. *Journal of environmental biology,* 24**,** 309-313.

ADIE, G. U. & OSIBANJO, O. 2009. Assessment of soil-pollution by slag from an automobile battery manufacturing plant in Nigeria. *African Journal of Environmental Science and Technology,* 3.

ADRIANO, D. C. 2001. Lead. *Trace Elements in Terrestrial Environments.* Springer.

ADRIANO, D. C., WENZEL, W. W., VANGRONSVELD, J. & BOLAN, N. S. 2004. Role of assisted natural remediation in environmental cleanup. *Geoderma,* 122**,** 121-142.

AELION, C. M., DAVIS, H. T., MCDERMOTT, S. & LAWSON, A. B. 2008. Metal concentrations in rural topsoil in South Carolina: potential for human health impact. *Science of the Total Environment,* 402**,** 149-156.

AGBAEZE, E., UDEH, S. & ONWUKA, I. 2015. Resolving Nigeria's dependency on oil-The derivation model. *Journal of African studies and development,* 7**,** 1.

AGBENIN, J. O. & WELP, G. 2012. Bioavailability of copper, cadmium, zinc, and lead in tropical savanna soils assessed by diffusive gradient in thin films (DGT) and ion exchange resin membranes. *Environmental monitoring and assessment,* 184**,** 2275-2284.

AGNELLO, A. C., BAGARD, M., VAN HULLEBUSCH, E. D., ESPOSITO, G. & HUGUENOT, D. 2016. Comparative bioremediation of heavy metals and petroleum hydrocarbons co-contaminated soil by natural attenuation, phytoremediation, bioaugmentation and bioaugmentation-assisted phytoremediation. *Science of the Total Environment,* 563**,** 693-703.

AHLUWALIA, S. S. & GOYAL, D. 2007. Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresource technology,* 98**,** 2243-2257.

AHMAD, A., BHAT, A. & BUANG, A. 2018. Biosorption of transition metals by freely suspended and Ca-alginate immobilised with Chlorella vulgaris: Kinetic and equilibrium modeling. *Journal of Cleaner Production,* 171**,** 1361-1375.

AHMARUZZAMAN, M. 2008. Adsorption of phenolic compounds on low-cost adsorbents: A review.

AHMED, M. J. K. & AHMARUZZAMAN, M. 2016. A review on potential usage of industrial waste materials for binding heavy metal ions from aqueous solutions. *Journal of Water Process Engineering,* 10**,** 39-47.

AJMAL, M., RAO, R. A. K., AHMAD, R. & AHMAD, J. 2000. Adsorption studies on Citrus reticulata (fruit peel of orange): removal and recovery of Ni (II) from electroplating wastewater. *Journal of hazardous materials,* 79**,** 117-131.

AKPOMIE, K. G. & DAWODU, F. A. 2016. Acid-modified montmorillonite for sorption of heavy metals from automobile effluent. *Beni-Suef University Journal of Basic and Applied Sciences,* 5**,** 1-12.

AKPOR, O. B. & MUCHIE, M. 2010. Remediation of heavy metals in drinking water and wastewater treatment systems: Processes and applications. *International Journal of Physical Sciences,* 5**,** 1807-1817.

AKSU, Z. 2001. Equilibrium and kinetic modelling of cadmium (II) biosorption by C. vulgaris in a batch system: effect of temperature. *Separation and Purification Technology,* 21**,** 285-294.

AKSU, Z. & İŞOĞLU, İ. A. 2005. Removal of copper (II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp. *Process Biochemistry,* 40**,** 3031-3044.

AL-RUB, F. A. A., KANDAH, M. & AL-DABAYBEH, N. 2002. Nickel removal from aqueous solutions using sheep manure wastes. *Engineering in life sciences,* 2**,** 111.
AL-SHAHRANI, S. S. 2014. Treatment of wastewater contaminated with cobalt using Saudi activated bentonite. *Alexandria Engineering Journal,* 53**,** 205-211.
ALI, H., KHAN, E. & SAJAD, M. A. 2013. Phytoremediation of heavy metals—concepts and applications. *Chemosphere,* 91**,** 869-881.
ALSLAIBI, T. M., ABUSTAN, I., AHMAD, M. A. & FOUL, A. A. 2013. Cadmium removal from aqueous solution using microwaved olive stone activated carbon. *Journal of Environmental Chemical Engineering,* 1**,** 589-599.
ALVAREZ, J. M., LOPEZ-VALDIVIA, L. M., NOVILLO, J., OBRADOR, A. & RICO, M. I. 2006. Comparison of EDTA and sequential extraction tests for phytoavailability prediction of manganese and zinc in agricultural alkaline soils. *Geoderma,* 132**,** 450-463.
ANANTHA, R. K. & KOTA, S. 2016. An evaluation of the major factors influencing the removal of copper ions using the egg shell (Dromaius novaehollandiae): chitosan (Agaricus bisporus) composite. *3 Biotech,* 6**,** 83.
ANASTOPOULOS, I., BHATNAGAR, A., HAMEED, B. H., OK, Y. S. & OMIROU, M. 2017. A review on waste-derived adsorbents from sugar industry for pollutant removal in water and wastewater. *Journal of Molecular Liquids*.
ANDRADE, L. H., RICCI, B. C., GROSSI, L. B., PIRES, W. L., AGUIAR, A. O. & AMARAL, M. C. S. 2017. Nanofiltration applied in gold mining effluent treatment: Evaluation of chemical cleaning and membrane stability. *Chemical Engineering Journal,* 323**,** 545-556.
ANNADURAI, G., JUANG, R. & LEE, D. 2003. Adsorption of heavy metals from water using banana and orange peels. *Water Science and Technology,* 47**,** 185-190.
ANODUADI, C. O., OKENWA, L. B., OKIEIMEN, F. E., TYOWUA, A. T. & UWUMARONGIE-ILORI, E. G. 2009. Metal immobilization in CCA contaminated soil using laterite and termite mound soil. Evaluation by chemical fractionation. *Nigerian journal of applied science,* 27**,** 77-87.
APPEL, C. & MA, L. 2002. Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils. *Journal of environmental quality,* 31**,** 581-589.
ARÁN, D., ANTELO, J., FIOL, S. & MACÍAS, F. 2016. Influence of feedstock on the copper removal capacity of waste-derived biochars. *Bioresource technology,* 212**,** 199-206.
ARECO, M. M., HANELA, S., DURAN, J. & DOS SANTOS AFONSO, M. 2012. Biosorption of Cu (II), Zn (II), Cd (II) and Pb (II) by dead biomasses of green alga Ulva lactuca and the development of a sustainable matrix for adsorption implementation. *Journal of hazardous materials,* 213**,** 123-132.
ARECO, M. M., RODRÍGUEZ, M. C. & DOS SANTOS AFONSO, M. 2014. Asterococcus superbus as a biosorbent of copper, zinc, cadmium and lead: adsorption isotherm and kinetic modelling. *International Journal of Environment and Health,* 7**,** 83-99.
ARIVOLI, S. & HENKUZHALI, M. 2008. Kinetic, mechanistic, thermodynamic and equilibrium studies on the adsorption of Rhodamine B by acid activated low cost carbon. *Journal of Chemistry,* 5**,** 187-200.
ASFARAM, A., GHAEDI, M., GOUDARZI, A. & RAJABI, M. 2015. Response surface methodology approach for optimization of simultaneous dye and metal ion ultrasound-assisted adsorption onto Mn doped Fe 3 O 4-NPs loaded on AC: kinetic and isothermal studies. *Dalton Transactions,* 44**,** 14707-14723.
AUSTRUY, A., SHAHID, M., XIONG, T., CASTREC, M., PAYRE, V., NIAZI, N. K., SABIR, M. & DUMAT, C. 2014. Mechanisms of metal-phosphates formation in the rhizosphere soils of pea and tomato: environmental and sanitary consequences. *Journal of Soils and Sediments,* 14**,** 666-678.

AWUAL, M. R., YAITA, T., EL-SAFTY, S. A., SHIWAKU, H., SUZUKI, S. & OKAMOTO, Y. 2013. Copper (II) ions capturing from water using ligand modified a new type mesoporous adsorbent. *Chemical Engineering Journal,* 221**,** 322-330.

AZIZULLAH, A., KHATTAK, M. N. K., RICHTER, P. & HÄDER, D.-P. 2011. Water pollution in Pakistan and its impact on public health—a review. *Environment international,* 37**,** 479-497.

BABEL, S. & KURNIAWAN, T. A. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of hazardous materials,* 97**,** 219-243.

BAHEMUKA, T. E. & MUBOFU, E. B. 1999. Heavy metals in edible green vegetables grown along the sites of the Sinza and Msimbazi rivers in Dar es Salaam, Tanzania. *Food Chemistry,* 66**,** 63-66.

BAILEY, S. E., OLIN, T. J., BRICKA, R. M. & ADRIAN, D. D. 1999. A review of potentially low-cost sorbents for heavy metals. *Water research,* 33**,** 2469-2479.

BAKIRCIOGLU, D., KURTULUS, Y. B. & İBAR, H. 2011. Comparison of extraction procedures for assessing soil metal bioavailability of to wheat grains. *Clean–Soil, Air, Water,* 39**,** 728-734.

BASHA, C. A., SOMASUNDARAM, M., KANNADASAN, T. & LEE, C. W. 2011. Heavy metals removal from copper smelting effluent using electrochemical filter press cells. *Chemical Engineering Journal,* 171**,** 563-571.

BASTA, N. & GRADWOHL, R. 2000. Estimation of Cd, Pb, and Zn bioavailability in smelter-contaminated soils by a sequential extraction procedure. *Journal of Soil Contamination,* 9**,** 149-164.

BECKETT, P. H. 1989. The use of extractants in studies on trace metals in soils, sewage sludges, and sludge-treated soils. *Advances in soil science.* Springer.

BEESLEY, L., MORENO-JIMÉNEZ, E. & GOMEZ-EYLES, J. L. 2010. Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. *Environmental pollution,* 158**,** 2282-2287.

BHATERIA, R. & DHAKA, R. 2017. Impact of electroplating effluent on growth of Triticum aestivum and Hordeum vulgare. *Environmental Technology & Innovation,* 8**,** 389-398.

BIAN, Y., BIAN, Z., ZHANG, J., DING, A., LIU, S., ZHENG, L. & WANG, H. 2015. Adsorption of cadmium ions from aqueous solutions by activated carbon with oxygen-containing functional groups. *Chinese Journal of Chemical Engineering,* 23**,** 1705-1711.

BILAL, M., SHAH, J. A., ASHFAQ, T., GARDAZI, S. M. H., TAHIR, A. A., PERVEZ, A., HAROON, H. & MAHMOOD, Q. 2013. Waste biomass adsorbents for copper removal from industrial wastewater—a review. *Journal of hazardous materials,* 263**,** 322-333.

BOLAN, N. S., ADRIANO, D. C., DURAISAMY, P. & MANI, A. 2003. Immobilization and phytoavailability of cadmium in variable charge soils. III. Effect of biosolid compost addition. *Plant and Soil,* 256**,** 231-241.

BOULDING, J. R. 1996. *EPA environmental assessment sourcebook*, CRC Press.

BRADY, N. C. & WEIL, R. R. 2004. Elements of the nature and properties of soils. Person Education. *Inc., Upper Saddle River, NJ, USA*.

BUENO, B. Y. M., TOREM, M. L., MOLINA, F. & DE MESQUITA, L. M. S. 2008. Biosorption of lead (II), chromium (III) and copper (II) by R. opacus: Equilibrium and kinetic studies. *Minerals Engineering,* 21**,** 65-75.

BULUT, Y. & ZEKI, T. E. Z. 2007. Removal of heavy metals from aqueous solution by sawdust adsorption. *Journal of Environmental Sciences,* 19**,** 160-166.

CAI, B., MA, J., YAN, G., DAI, X., LI, M. & GUO, S. 2016. Comparison of phytoremediation, bioaugmentation and natural attenuation for remediating saline soil contaminated by heavy crude oil. *Biochemical engineering journal,* 112**,** 170-177.

CAMBIER, P., POT, V., MERCIER, V., MICHAUD, A., BENOIT, P., REVALLIER, A. & HOUOT, S. 2014. Impact of long-term organic residue recycling in agriculture on soil solution

composition and trace metal leaching in soils. *Science of the Total Environment,* 499**,** 560-573.
CAMPBELL, P. G. C., TESSIER, A. & TURNER, D. R. 1995. *Metal speciation and bioavailability in aquatic systems*, John Wiley & Sons: Chichester, United Kingdom.
CAO, S., DUAN, X., ZHAO, X., WANG, B., MA, J., FAN, D., SUN, C., HE, B., WEI, F. & JIANG, G. 2015. Health risk assessment of various metal (loid) s via multiple exposure pathways on children living near a typical lead-acid battery plant, China. *Environmental Pollution,* 200**,** 16-23.
CAO, Y. & LI, X. 2014. Adsorption of graphene for the removal of inorganic pollutants in water purification: a review. *Adsorption,* 20**,** 713-727.
CARBONELL, R. G. 1986. Adsorption technology: A step-by-step approach to process evaluation and application (chemical industries series, vol. 19). Edited by Frank L. Slejko, Marcel Dekker, inc., 1985, 240 pp., $55.00 (US and Canada); $66.00 (all other countries). *AIChE Journal,* 32**,** 875-876.
CAROLIN, C. F., KUMAR, P. S., SARAVANAN, A., JOSHIBA, G. J. & NAUSHAD, M. 2017. Efficient Techniques for the Removal of Toxic Heavy Metals from Aquatic Environment: A Review. *Journal of Environmental Chemical Engineering*.
CASTRO, R. S. D., CAETANO, L., FERREIRA, G., PADILHA, P. M., SAEKI, M. J., ZARA, L. F., MARTINES, M. A. U. & CASTRO, G. R. 2011. Banana peel applied to the solid phase extraction of copper and lead from river water: preconcentration of metal ions with a fruit waste. *Industrial & Engineering Chemistry Research,* 50**,** 3446-3451.
CAVACO, S. A., FERNANDES, S., QUINA, M. M. & FERREIRA, L. M. 2007. Removal of chromium from electroplating industry effluents by ion exchange resins. *Journal of hazardous materials,* 144**,** 634-638.
CHEN, M., XU, P., ZENG, G., YANG, C., HUANG, D. & ZHANG, J. 2015. Bioremediation of soils contaminated with polycyclic aromatic hydrocarbons, petroleum, pesticides, chlorophenols and heavy metals by composting: applications, microbes and future research needs. *Biotechnology Advances,* 33**,** 745-755.
CHOI, Y., CHO, Y.-M. & LUTHY, R. G. 2014. In situ sequestration of hydrophobic organic contaminants in sediments under stagnant contact with activated carbon. 1. Column studies. *Environmental science & technology,* 48**,** 1835-1842.
CHRISTL, I. & KRETZSCHMAR, R. 2001. Relating ion binding by fulvic and humic acids to chemical composition and molecular size. 1. Proton binding. *Environmental science & technology,* 35**,** 2505-2511.
CHRONOPOULOS, J., HAIDOUTI, C., CHRONOPOULOU-SERELI, A. & MASSAS, I. 1997. Variations in plant and soil lead and cadmium content in urban parks in Athens, Greece. *Science of the Total Environment,* 196**,** 91-98.
CHU, L., LIU, C., ZHOU, G., XU, R., TANG, Y., ZENG, Z. & LUO, S. 2015. A double network gel as low cost and easy recycle adsorbent: Highly efficient removal of Cd (II) and Pb (II) pollutants from wastewater. *Journal of hazardous materials,* 300**,** 153-160.
CHUKWU, O. 2008. Analysis of groundwater pollution from abattoir waste in Minna, Nigeria. *Research Journal of Dairy Sciences,* 2**,** 74-77.
COWEN, D. V. 1984. Flowering Trees and Shrubs in India, Bombay: Thacker and Co. Ltd. *Agroforest Today,* 6.
CRINI, G. 2005. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in polymer science,* 30**,** 38-70.
CUI, L., LI, L., ZHANG, A., PAN, G., BAO, D. & CHANG, A. 2011. Biochar amendment greatly reduces rice Cd uptake in a contaminated paddy soil: a two-year field experiment. *BioResources,* 6**,** 2605-2618.
D'AVILA, J. S., MATOS, C. M. & CAVALCANTI, M. R. 1992. Heavy metals removal from wastewater by using activated peat. *Water Science and Technology,* 26**,** 2309-2312.

DAS, A. K., CHAKRABORTY, R., CERVERA, M. L. & DE LA GUARDIA, M. 1995. Metal speciation in solid matrices. *Talanta,* 42**,** 1007-1030.

DAS, D. B. & NASSEHI, V. 2001. LANDFLOW: a 3D finite volume model of combined free and porous flow of water in contaminated land sites. *Water science and technology,* 43**,** 55-64.

DAVISON, W. & ZHANG, H. 2012. Progress in understanding the use of diffusive gradients in thin films (DGT)–back to basics. *Environmental Chemistry,* 9**,** 1-13.

DAVLSON, W. & ZHANG, H. 1994. In situspeciation measurements of trace components in natural waters using thin-film gels. *Nature,* 367**,** 546-548.

DE BARROS AMORIM, M. J., RÖMBKE, J., SCHALLNAß, H. J. & SOARES, A. M. V. M. 2005. Effect of soil properties and aging on the toxicity of copper for Enchytraeus albidus, Enchytraeus luxuriosus, and Folsomia candida. *Environmental Toxicology and Chemistry,* 24**,** 1875-1885.

DE GISI, S., LOFRANO, G., GRASSI, M. & NOTARNICOLA, M. 2016. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: a review. *Sustainable Materials and Technologies,* 9**,** 10-40.

DEMIRBAS, A. 2008. Heavy metal adsorption onto agro-based waste materials: a review. *Journal of hazardous materials,* 157**,** 220-229.

DI BONITO, M., BREWARD, N., CROUT, N., SMITH, B. & YOUNG, S. 2008. Overview of selected soil pore water extraction methods for the determination of potentially toxic elements in contaminated soils: operational and technical aspects. *Environmental geochemistry.Site characterization, data analysis and case histories.Nottingham: Elsevier***,** 213-249.

DIXIT, S. S., DIXIT, A. S. & SMOL, J. P. 1992a. Assessment of changes in lake water chemistry in Sudbury area lakes since preindustrial times. *Canadian Journal of Fisheries and Aquatic Sciences,* 49**,** 8-16.

DIXIT, S. S., SMOL, J. P., KINGSTON, J. C. & CHARLES, D. F. 1992b. Diatoms: powerful indicators of environmental change. *Environmental science & technology,* 26**,** 22-33.

DUBEY, A. & SHIWANI, S. 2012. Adsorption of lead using a new green material obtained from Portulaca plant. *International Journal of Environmental Science and Technology,* 9**,** 15-20.

DUDKA, S. & ADRIANO, D. C. 1997. Environmental impacts of metal ore mining and processing: a review. *Journal of environmental quality,* 26**,** 590-602.

DUDKA, S., PONCE-HERNANDEZ, R., TATE, G. & HUTCHINSON, T. C. 1996. Forms of Cu, Ni, and Zn in soils of Sudbury, Ontario and the metal concentrations in plants. *Water, Air, & Soil Pollution,* 90**,** 531-542.

DURUIBE, J. O., OGWUEGBU, M. O. C. & EGWURUGWU, J. N. 2007. Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences,* 2**,** 112-118.

EGILA, J. N., DAUDA, B. E. N. & JIMOH, T. 2010. Biosorptive removal of cobalt (II) ions from aqueous solution by Amaranthus hydridus L. stalk wastes. *African Journal of Biotechnology,* 9**,** 8192-8198.

EL-BAYAA, A. A., BADAWY, N. A. & ALKHALIK, E. A. 2009. Effect of ionic strength on the adsorption of copper and chromium ions by vermiculite pure clay mineral. *Journal of hazardous materials,* 170**,** 1204-1209.

ELAIGWU, S. E., USMAN, L. A., AWOLOLA, G. V., ADEBAYO, G. B. & AJAYI, R. M. K. 2009. Adsorption of Pb (II) from aqueous solution by activated carbon prepared from cow dung. *Adv.Natural Appl.Sci,* 3**,** 442-446.

ERNSTBERGER, H., DAVISON, W., ZHANG, H., TYE, A. & YOUNG, S. 2002. Measurement and dynamic modeling of trace metal mobilization in soils using DGT and DIFS. *Environmental science & technology,* 36**,** 349-354.

ERNSTBERGER, H., ZHANG, H., TYE, A., YOUNG, S. & DAVISON, W. 2005. Desorption kinetics of Cd, Zn, and Ni measured in soils by DGT. *Environmental science & technology,* 39**,** 1591-1597.

EWECHAROEN, A., THIRAVETYAN, P. & NAKBANPOTE, W. 2008. Comparison of nickel adsorption from electroplating rinse water by coir pith and modified coir pith. *Chemical Engineering Journal,* 137**,** 181-188.

FAROOQ, U., KHAN, M. A., ATHAR, M. & KOZINSKI, J. A. 2011. Effect of modification of environmentally friendly biosorbent wheat (Triticum aestivum) on the biosorptive removal of cadmium (II) ions from aqueous solution. *Chemical Engineering Journal,* 171**,** 400-410.

FAROOQ, U., KOZINSKI, J. A., KHAN, M. A. & ATHAR, M. 2010. Biosorption of heavy metal ions using wheat based biosorbents–a review of the recent literature. *Bioresource technology,* 101**,** 5043-5053.

FENG, Y., GONG, J.-L., ZENG, G.-M., NIU, Q.-Y., ZHANG, H.-Y., NIU, C.-G., DENG, J.-H. & YAN, M. 2010. Adsorption of Cd (II) and Zn (II) from aqueous solutions using magnetic hydroxyapatite nanoparticles as adsorbents. *Chemical Engineering Journal,* 162**,** 487-494.

FERRARO, A., VAN HULLEBUSCH, E. D., HUGUENOT, D., FABBRICINO, M. & ESPOSITO, G. 2015. Application of an electrochemical treatment for EDDS soil washing solution regeneration and reuse in a multi-step soil washing process: case of a Cu contaminated soil. *Journal of environmental management,* 163**,** 62-69.

FESTUS, A. A., ELVIS, O. A. & MORAYO, A. B. 2013. Equilibrium Sorption of Lead and Nickel from Solutions by Flame of the Forest (Delonix regia) Pods: Kinetics and Isothermic Study. *Journal of Environmental Protection,* 4**,** 261.

FIJAŁKOWSKI, K., KACPRZAK, M., GROBELAK, A. & PLACEK, A. 2012. The influence of selected soil parameters on the mobility of heavy metals in soils. *Inżynieria i Ochrona środowiska,* 15**,** 81-92.

FLORENCE, T. M. 1986. Electrochemical approaches to trace element speciation in waters. A review. *Analyst,* 111**,** 489-505.

FU, F. & WANG, Q. 2011. Removal of heavy metal ions from wastewaters: a review. *Journal of environmental management,* 92**,** 407-418.

GADD, G. M. 2000. Bioremedial potential of microbial mechanisms of metal mobilization and immobilization. *Current opinion in biotechnology,* 11**,** 271-279.

GADD, G. M. 2009. Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. *Journal of Chemical Technology and Biotechnology,* 84**,** 13-28.

GALADIMA, A., GARBA, Z., LEKE, L., ALMUSTAPHA, M. & ADAM, I. 2011. Domestic water pollution among local communities in Nigeria-causes and consequences. *European Journal of Scientific Research,* 52**,** 592-603.

GARI, L. 2002. Arabic treatises on environmental pollution up to the end of the thirteenth century. *Environment and History,* 8**,** 475-488.

GHODBANE, I. & HAMDAOUI, O. 2008. Removal of mercury (II) from aqueous media using eucalyptus bark: Kinetic and equilibrium studies. *Journal of hazardous materials,* 160**,** 301-309.

GHOSH, M. & SINGH, S. 2005. A review on phytoremediation of heavy metals and utilization of it's by products. *Asian J Energy Environ,* 6**,** 18.

GOMEZ-EYLES, J. L., YUPANQUI, C., BECKINGHAM, B., RIEDEL, G., GILMOUR, C. & GHOSH, U. 2013. Evaluation of biochars and activated carbons for in situ remediation of sediments impacted with organics, mercury, and methylmercury. *Environmental science & technology,* 47**,** 13721-13729.

GÖNEN, F. & SERIN, D. S. 2012. Adsorption study on orange peel: removal of Ni (II) ions from aqueous solution. *African Journal of Biotechnology,* 11**,** 1250-1258.

GOVIND, P. & MADHURI, S. 2014. Heavy metals causing toxicity in animals and fishes. *Research Journal of Animal, Veterinary and Fishery Sciences,* 2**,** 17-23.
GRÄFE, M., DONNER, E., COLLINS, R. N. & LOMBI, E. 2014. Speciation of metal (loid) s in environmental samples by X-ray absorption spectroscopy: A critical review. *Analytica Chimica Acta,* 822**,** 1-22.
GRAMLICH, A., TANDY, S., GAUGGEL, C., LÓPEZ, M., PERLA, D., GONZALEZ, V. & SCHULIN, R. 2018. Soil cadmium uptake by cocoa in Honduras. *Science of The Total Environment,* 612**,** 370-378.
GREIPSSON, S. 2011. Phytoremediation. *Nature Education Knowledge,* 3**,** 7.
GU, X., LIU, Z., WANG, X., LUO, J., ZHANG, H., DAVISON, W., MA, L. Q. & XUE, Y. 2017. Coupling biological assays with diffusive gradients in thin-films technique to study the biological responses of Eisenia fetida to cadmium in soil. *Journal of hazardous materials,* 339**,** 340-346.
GUAN, D.-X., ZHENG, J.-L., LUO, J., ZHANG, H., DAVISON, W. & MA, L. Q. 2017. A diffusive gradients in thin-films technique for the assessment of bisphenols desorption from soils. *Journal of hazardous materials,* 331**,** 321-328.
GUO, X., WEI, Z., WU, Q., LI, C., QIAN, T. & ZHENG, W. 2016. Effect of soil washing with only chelators or combining with ferric chloride on soil heavy metal removal and phytoavailability: field experiments. *Chemosphere,* 147**,** 412-419.
GUPTA, S. K. & ATEN, C. 1993. Comparison and evaluation of extraction media and their suitability in a simple model to predict the biological relevance of heavy metal concentrations in contaminated soils. *International journal of environmental analytical chemistry,* 51**,** 25-46.
GUTHA, Y., MUNAGAPATI, V. S., ALLA, S. R. & ABBURI, K. 2011. Biosorptive removal of Ni (II) from aqueous solution by Caesalpinia bonducella seed powder. *Separation Science and Technology,* 46**,** 2291-2297.
HALL, K. R., EAGLETON, L. C., ACRIVOS, A. & VERMEULEN, T. 1966. Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Industrial & Engineering Chemistry Fundamentals,* 5**,** 212-223.
HARPER, M. P., DAVISON, W. & TYCH, W. 2000. DIFS—a modelling and simulation tool for DGT induced trace metal remobilisation in sediments and soils. *Environmental Modelling & Software,* 15**,** 55-66.
HARPER, M. P., DAVISON, W., ZHANG, H. & TYCH, W. 1998. Kinetics of metal exchange between solids and solutions in sediments and soils interpreted from DGT measured fluxes. *Geochimica et Cosmochimica Acta,* 62**,** 2757-2770.
HASANAH, A. N., RIZKIANA, F. & RAHAYU, D. 2012. Banana Peels and Stem (Musa x paradisiaca Linn.) as Biosorbent of Copper in Textile Industry Wastewater. *Res.J.Pharm.Biol.Chem.Sci,* 3**,** 1171.
HASAR, H. 2003. Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from almond husk. *Journal of hazardous materials,* 97**,** 49-57.
HASHEM, M. A. 2007. Adsorption of lead ions from aqueous solution by okra wastes. *International Journal of Physical Sciences,* 2**,** 178-184.
HELMER, R., HESPANHOL, I. & ORGANIZATION, W. H. 1997. Water pollution control: a guide to the use of water quality management principles.
HELMKE, P. A., SALAM, A. K. & LI, Y. 1997. Measurement and behavior of indigenous levels of the free-hydrated cations of Cu, Zn and Cd in the soil water system. *Colloques de l'INRA (France)*.
HEMA, M. & ARIVOLI, S. 2007. Comparative study on the adsorption kinetics and thermodynamics of dyes onto acid activated low cost carbon. *International Journal of Physical Sciences,* 2**,** 10-17.
HENRY, J. R. 2000. In An Overview of Phytoremediation of Lead and Mercury. NNEMS Report, Washington DC, 3-9. *Motesharezadeh, B.et al***,** 1099-1105.

HINRICHSEN, D. & TACIO, H. 2002. The coming freshwater crisis is already here. *The linkages between population and water.Washington, DC: Woodrow Wilson International Center for Scholars*, 1-26.
HO, Y.-S. & MCKAY, G. 1998. Sorption of dye from aqueous solution by peat. *Chemical Engineering Journal,* 70, 115-124.
HO, Y.-S. & MCKAY, G. 1999a. Pseudo-second order model for sorption processes. *Process biochemistry,* 34, 451-465.
HO, Y. S. & MCKAY, G. 1999b. Comparative sorption kinetic studies of dye and aromatic compounds onto fly ash. *Journal of Environmental Science & Health Part A,* 34, 1179-1204.
HO, Y. S. & MCKAY, G. 1999c. The sorption of lead (II) ions on peat. *Water research,* 33, 578-584.
HOODA, P., MCNULTY, D., ALLOWAY, B. & AITKEN, M. 1997. Plant availability of heavy metals in soils previously amended with heavy applications of sewage sludge. *Journal of the Science of Food and Agriculture,* 73, 446-454.
HOODA, P. S. 2010. Assessing bioavailability of soil trace elements. *Trace Elements in Soils*, 227-265.
HOODA, P. S. & ZHANG, H. 2008. DGT measurements to predict metal bioavailability in soils. *Developments in Soil Science,* 32, 169-185.
HOODA, P. S., ZHANG, H., DAVISON, W. & EDWARDS, A. C. 1999. Measuring bioavailable trace metals by diffusive gradients in thin films (DGT): soil moisture effects on its performance in soils. *European Journal of Soil Science,* 50, 285-294.
HOSSAIN, M. A., NGO, H. H., GUO, W. S. & NGUYEN, T. V. 2012a. Palm oil fruit shells as biosorbent for copper removal from water and wastewater: experiments and sorption models. *Bioresource technology,* 113, 97-101.
HOSSAIN, M. A., NGO, H. H., GUO, W. S. & SETIADI, T. 2012b. Adsorption and desorption of copper (II) ions onto garden grass. *Bioresource technology,* 121, 386-395.
HU, X., ZHAO, M., SONG, G. & HUANG, H. 2011. Modification of pineapple peel fibre with succinic anhydride for Cu2 , Cd2 and Pb2 removal from aqueous solutions. *Environmental technology,* 32, 739-746.
IBETO, C. & OKOYE, C. 2010. High levels of Heavy metals in Blood of Urban population in Nigeria. *Research Journal of Environmental Sciences,* 4, 371-382.
IBRAHIM, M. M., NGAH, W. W., NORLIYANA, M., DAUD, W. W., RAFATULLAH, M., SULAIMAN, O. & HASHIM, R. 2010. A novel agricultural waste adsorbent for the removal of lead (II) ions from aqueous solutions. *Journal of Hazardous Materials,* 182, 377-385.
IBRAHIM, W. M., HASSAN, A. F. & AZAB, Y. A. 2016. Biosorption of toxic heavy metals from aqueous solution by Ulva lactuca activated carbon. *Egyptian Journal of Basic and Applied Sciences,* 3, 241-249.
JÄRUP, L. 2003. Hazards of heavy metal contamination. *British medical bulletin,* 68, 167-182.
JIANG, J., XU, R.-K., JIANG, T.-Y. & LI, Z. 2012. Immobilization of Cu (II), Pb (II) and Cd (II) by the addition of rice straw derived biochar to a simulated polluted Ultisol. *Journal of hazardous materials,* 229, 145-150.
JIANG, X. J., LUO, Y. M., ZHAO, Q. G., BAKER, A. J. M., CHRISTIE, P. & WONG, M. H. 2003. Soil Cd availability to Indian mustard and environmental risk following EDTA addition to Cd-contaminated soil. *Chemosphere,* 50, 813-818.
JINXIA, L. I., MEI, H., XIUQIN, Y. I. N. & JILIANG, L. I. U. 2010. Effects of the accumulation of the rare earth elements on soil macrofauna community. *Journal of Rare Earths,* 28, 957-964.
KABATA-PENDIAS, A. 1993. Behavioural properties of trace metals in soils. *Applied geochemistry,* 8, 3-9.
KABATA-PENDIAS, A. 2004. Soil–plant transfer of trace elements—an environmental issue. *Geoderma,* 122, 143-149.

KANG, Y., GUO, Z., ZHANG, J., XIE, H., LIU, H. & ZHANG, C. 2016. Enhancement of Ni (II) removal by urea-modified activated carbon derived from Pennisetum alopecuroides with phosphoric acid activation. *Journal of the Taiwan Institute of Chemical Engineers,* 60**,** 335-341.

KAPOOR, A. & VIRARAGHAVAN, T. 1995. Fungal biosorption—an alternative treatment option for heavy metal bearing wastewaters: a review. *Bioresource technology,* 53**,** 195-206.

KARAMI, N., CLEMENTE, R., MORENO-JIMÉNEZ, E., LEPP, N. W. & BEESLEY, L. 2011. Efficiency of green waste compost and biochar soil amendments for reducing lead and copper mobility and uptake to ryegrass. *Journal of hazardous materials,* 191**,** 41-48.

KASCHL, A., RÖMHELD, V. & CHEN, Y. 2002. Cadmium binding by fractions of dissolved organic matter and humic substances from municipal solid waste compost. *Journal of environmental quality,* 31**,** 1885-1892.

KHALID, S., SHAHID, M., NIAZI, N. K., MURTAZA, B., BIBI, I. & DUMAT, C. 2017. A comparison of technologies for remediation of heavy metal contaminated soils. *Journal of Geochemical Exploration,* 182**,** 247-268.

KHAN, M. A., CHATTHA, M. R., FAROOQ, K., JAWED, M. A., FAROOQ, M., IMRAN, M., IFTKHAR, M. & KASANA, M. I. 2015. Effect of farmyard manure levels and NPK applications on the pea plant growth, pod yield and quality. *Life Sciences International Journal,* 9**,** 3178-3181.

KHUZESTANI, R. B. & SOURI, B. 2013. Evaluation of heavy metal contamination hazards in nuisance dust particles, in Kurdistan Province, western Iran. *Journal of Environmental Sciences,* 25**,** 1346-1354.

KIM, C. S., BLOOM, N. S., RYTUBA, J. J. & BROWN, G. E. 2003. Mercury speciation by X-ray absorption fine structure spectroscopy and sequential chemical extractions: a comparison of speciation methods. *Environmental science & technology,* 37**,** 5102-5108.

KONG, S., LU, B., JI, Y., ZHAO, X., CHEN, L., LI, Z., HAN, B. & BAI, Z. 2011. Levels, risk assessment and sources of PM 10 fraction heavy metals in four types dust from a coal-based city. *Microchemical Journal,* 98**,** 280-290.

KRISHNAMURTI, G. S. R., CIESLINSKI, G., HUANG, P. M. & VAN REES, K. C. J. 1997. Kinetics of cadmium release from soils as influenced by organic acids: implication in cadmium availability. *Journal of environmental quality,* 26**,** 271-277.

KULIKOWSKA, D., GUSIATIN, Z. M., BUŁKOWSKA, K. & KLIK, B. 2015. Feasibility of using humic substances from compost to remove heavy metals (Cd, Cu, Ni, Pb, Zn) from contaminated soil aged for different periods of time. *Journal of hazardous materials,* 300**,** 882-891.

KUMAR, M. & PURI, A. 2012. A review of permissible limits of drinking water. *Indian journal of occupational and environmental medicine,* 16**,** 40-44.

KUMAR, U. & BANDYOPADHYAY, M. 2006. Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresource technology,* 97**,** 104-109.

KUMPIENE, J., LAGERKVIST, A. & MAURICE, C. 2008. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments–a review. *Waste Management,* 28**,** 215-225.

KURNIAWAN, T. A., CHAN, G. Y. S., LO, W.-H. & BABEL, S. 2006. Physico–chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal,* 118**,** 83-98.

LANGMUIR, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical Society,* 40**,** 1361-1403.

LANNO, R., WELLS, J., CONDER, J., BRADHAM, K. & BASTA, N. 2004. The bioavailability of chemicals in soil for earthworms. *Ecotoxicology and environmental safety,* 57**,** 39-47.

LASAT, M. 2000. Phytoextraction of metals from contaminated soil: a review of plant/soil/metal interaction and assessment of pertinent agronomic issues. *J Hazard Subst Res,* 2**,** 1-25.
LEE, C. S.-L., LI, X., SHI, W., CHEUNG, S. C.-N. & THORNTON, I. 2006. Metal contamination in urban, suburban, and country park soils of Hong Kong: a study based on GIS and multivariate statistics. *Science of the Total Environment,* 356**,** 45-61.
LEE, M., PAIK, I. S., KIM, I., KANG, H. & LEE, S. 2007. Remediation of heavy metal contaminated groundwater originated from abandoned mine using lime and calcium carbonate. *Journal of hazardous materials,* 144**,** 208-214.
LEE, Y.-C. & CHANG, S.-P. 2011. The biosorption of heavy metals from aqueous solution by Spirogyra and Cladophora filamentous macroalgae. *Bioresource technology,* 102**,** 5297-5304.
LEHMANN, J. & JOSEPH, S. 2015. *Biochar for environmental management: science, technology and implementation*, Routledge.
LEHTO, N. J., DAVISON, W., TYCH, W. & ZHANG, H. 2008. Quantitative assessment of soil parameter (K D and T C) estimation using DGT measurements and the 2D DIFS model. *Chemosphere,* 71**,** 795-801.
LEYVAL, C. & BERTHELIN, J. 1993. Rhizodeposition and net release of soluble organic compounds by pine and beech seedlings inoculated with rhizobacteria and ectomycorrhizal fungi. *Biology and Fertility of Soils,* 15**,** 259-267.
LI, L., WU, H., VAN GESTEL, C. A. M., PEIJNENBURG, W. J. G. M. & ALLEN, H. E. 2014a. Soil acidification increases metal extractability and bioavailability in old orchard soils of Northeast Jiaodong Peninsula in China. *Environmental Pollution,* 188**,** 144-152.
LI, Z., MA, Z., VAN DER KUIJP, T. J., YUAN, Z. & HUANG, L. 2014b. A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. *Science of the Total Environment,* 468**,** 843-853.
LIU, Y., CAO, Q., LUO, F. & CHEN, J. 2009. Biosorption of Cd 2 , Cu 2 , Ni 2 and Zn 2 ions from aqueous solutions by pretreated biomass of brown algae. *Journal of hazardous materials,* 163**,** 931-938.
LÓPEZ, M. L., PERALTA-VIDEA, J. R., BENITEZ, T. & GARDEA-TORRESDEY, J. L. 2005. Enhancement of lead uptake by alfalfa (Medicago sativa) using EDTA and a plant growth promoter. *Chemosphere,* 61**,** 595-598.
LU, H., ZHANG, W., YANG, Y., HUANG, X., WANG, S. & QIU, R. 2012. Relative distribution of Pb 2 sorption mechanisms by sludge-derived biochar. *Water research,* 46**,** 854-862.
LU, R. K. 2000. Soil agrochemistry and analytical methods. *Chinese Agricultural Science and Technology Press, Beijing (in Chinese)*.
MA, W., EDELMAN, T., VAN BEERSUM, I. & JANS, T. 1983. Uptake of cadmium, zinc, lead, and copper by earthworms near a zinc-smelting complex: influence of soil pH and organic matter. *Bulletin of Environmental Contamination and Toxicology,* 30**,** 424-427.
MAKINO, T., TAKANO, H., KAMIYA, T., ITOU, T., SEKIYA, N., INAHARA, M. & SAKURAI, Y. 2008. Restoration of cadmium-contaminated paddy soils by washing with ferric chloride: Cd extraction mechanism and bench-scale verification. *Chemosphere,* 70**,** 1035-1043.
MALLAMPATI, S. R., MITOMA, Y., OKUDA, T., SIMION, C. & LEE, B. K. 2015. Dynamic immobilization of simulated radionuclide 133 Cs in soil by thermal treatment/vitrification with nanometallic Ca/CaO composites. *Journal of environmental radioactivity,* 139**,** 118-124.
MAO, X., JIANG, R., XIAO, W. & YU, J. 2015. Use of surfactants for the remediation of contaminated soils: a review. *Journal of hazardous materials,* 285**,** 419-435.
MARSCHNER, H. & RÖMHELD, V. 1983. In vivo measurement of root-induced pH changes at the soil-root interface: effect of plant species and nitrogen source. *Zeitschrift für Pflanzenphysiologie,* 111**,** 241-251.

MARTÍNEZ, C. E. & MCBRIDE, M. B. 1999. Dissolved and labile concentrations of Cd, Cu, Pb, and Zn in aged ferrihydrite− organic matter systems. *Environmental science & technology,* 33**,** 745-750.
MCKAY, G., HO, Y. S. & NG, J. C. Y. 1999. Biosorption of copper from waste waters: a review. *Separation and Purification Methods,* 28**,** 87-125.
MCLAUGHLIN, M. J., PALMER, L. T., TILLER, K. G., BEECH, T. A. & SMART, M. K. 1994. Increased soil salinity causes elevated cadmium concentrations in field-grown potato tubers. *Journal of environmental quality,* 23**,** 1013-1018.
MCLAUGHLIN, M. J., ZARCINAS, B. A., STEVENS, D. P. & COOK, N. 2000. Soil testing for heavy metals. *Communications in Soil Science & Plant Analysis,* 31**,** 1661-1700.
MÉNDEZ, A., GÓMEZ, A., PAZ-FERREIRO, J. & GASCÓ, G. 2012. Effects of sewage sludge biochar on plant metal availability after application to a Mediterranean soil. *Chemosphere,* 89**,** 1354-1359.
MERRINGTON, G. & ALLOWAY, B. J. 1994. The flux of Cd, Cu, Pb and Zn in mining polluted soils. *Water, air, and soil pollution,* 73**,** 333-344.
MESA, A. C. & SPOKAS, K. 2011. Impacts of biochar (black carbon) additions on the sorption and efficacy of herbicides. *Herbicides and Environment.* InTech.
MIER, M. V., CALLEJAS, R. L., GEHR, R., CISNEROS, B. E. J. & ALVAREZ, P. J. J. 2001. Heavy metal removal with mexican clinoptilolite:: multi-component ionic exchange. *Water research,* 35**,** 373-378.
MODI, A., MISHRA, V., BHATT, A., JAIN, A., MANSOORI, M. H., GURNANY, E. & KUMAR, V. 2016. Delonix regia: historic perspectives and modern phytochemical and pharmacological researches. *Chinese journal of natural medicines,* 14**,** 31-39.
MONTERO, N., BELZUNCE-SEGARRA, M. J., GONZALEZ, J. L., LARRETA, J. & FRANCO, J. 2012. Evaluation of diffusive gradients in thin-films (DGTs) as a monitoring tool for the assessment of the chemical status of transitional waters within the Water Framework Directive. *Marine pollution bulletin,* 64**,** 31-39.
MORENO-TOVAR, R., TERRÉS, E. & RANGEL-MENDEZ, J. R. 2014. Oxidation and EDX elemental mapping characterization of an ordered mesoporous carbon: Pb (II) and Cd (II) removal. *Applied Surface Science,* 303**,** 373-380.
MORLEY, G. F. & GADD, G. M. 1995. Sorption of toxic metals by fungi and clay minerals. *Mycological Research,* 99**,** 1429-1438.
MORTENSEN, J. 1963. Complexing of metals by soil organic matter. *Soil Science Society of America Journal,* 27**,** 179-186.
MOUBARIK, A. & GRIMI, N. 2015. Valorization of olive stone and sugar cane bagasse by-products as biosorbents for the removal of cadmium from aqueous solution. *Food Research International,* 73**,** 169-175.
MULLIGAN, C. N., YONG, R. N. & GIBBS, B. F. 2001. Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Engineering Geology,* 60**,** 193-207.
MUSTAPHA, S., DAUDA, B. E. N., NDAMITSO, M. M., MATHEW, T. J., BASSEY, U. & MUHAMMED, S. S. 2014. Biosorption of Copper from Aqueous Solutions by Raw and Activated Spines of Bombax buonopozense: Equilibrium, Kinetics and Thermodynamic Studies. *International Research Journal of Pure and Applied Chemistry,* 4**,** 887.
NETZER, A. & HUGHES, D. E. 1984. Adsorption of copper, lead and cobalt by activated carbon. *Water research,* 18**,** 927-933.
NGUYEN, T. A. H., NGO, H. H., GUO, W. S., ZHANG, J., LIANG, S., YUE, Q. Y., LI, Q. & NGUYEN, T. V. 2013. Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. *Bioresource technology,* 148**,** 574-585.
NIAZI, N. K., BASHIR, S., BIBI, I., MURTAZA, B., SHAHID, M., JAVED, M. T., SHAKOOR, M. B., SAQIB, Z. A., NAWAZ, M. F. & ASLAM, Z. 2016. Phytoremediation of arsenic-

contaminated soils using arsenic hyperaccumulating ferns. *Phytoremediation.* Springer.
NICHOLSON, F., SMITH, S., ALLOWAY, B., CARLTON-SMITH, C. & CHAMBERS, B. 2003. An inventory of heavy metals inputs to agricultural soils in England and Wales. *Science of the total environment,* 311**,** 205-219.
NJOKU, V. O., AYUK, A. A., EJIKE, E. E., OGUZIE, E. E., DURU, C. E. & BELLO, O. S. 2011. Cocoa pod husk as a low cost biosorbent for the removal of Pb (II) and Cu (II) from aqueous solutions. *Australian Journal of Basic and Applied Sciences,* 5**,** 101-110.
NOLAN, A. L., LOMBI, E. & MCLAUGHLIN, M. J. 2003. Metal bioaccumulation and toxicity in soils—why bother with speciation? *Australian Journal of Chemistry,* 56**,** 77-91.
NOLAN, A. L., ZHANG, H. & MCLAUGHLIN, M. J. 2005. Prediction of zinc, cadmium, lead, and copper availability to wheat in contaminated soils using chemical speciation, diffusive gradients in thin films, extraction, and isotopic dilution techniques. *Journal of environmental quality,* 34**,** 496-507.
NOREEN, M., SHAHID, M., IQBAL, M. & NISAR, J. 2017. Measurement of cytotoxicity and heavy metal load in drains water receiving textile effluents and drinking water in vicinity of drains. *Measurement,* 109**,** 88-99.
NRIAGU, J. O. 1996. A history of global metal pollution. *Science,* 272**,** 223.
OFOMAJA, A. E., NAIDOO, E. B. & MODISE, S. J. 2010. Biosorption of copper (II) and lead (II) onto potassium hydroxide treated pine cone powder. *Journal of environmental management,* 91**,** 1674-1685.
OGUNKUNLE, C. O. & FATOBA, P. O. 2013. Pollution Loads and the Ecological Risk Assessment of Soil Heavy Metals around a Mega Cement Factory in Southwest Nigeria. *Polish Journal of Environmental Studies,* 22.
OGUNLEYE, O. O., AJALA, M. A. & AGARRY, S. E. 2014. Evaluation of Biosorptive Capacity of Banana (Musa paradisiaca) Stalk for Lead (II) Removal from Aqueous Solution. *Journal of Environmental Protection,* 5**,** 1451.
OKIEIMEN, F. E., MAYA, A. O. & ORIAKHI, C. O. 1988. Sorption of cadmium, lead and zinc ions on sulphur-containing chemically modified cellulosic materials. *International journal of environmental analytical chemistry,* 32**,** 23-27.
OKORONKWO, A. E., ADEBAYO, A. O. & OMOTUNDE, O. I. 2013. Sorptive removal of cadmium from aqueous solutions by Delonix regia derived lignin: effect of amination. *Desalination and Water Treatment,* 51**,** 5026-5034.
ÖRNEK, A., ÖZACAR, M. & ŞENGIL, İ. A. 2007. Adsorption of lead onto formaldehyde or sulphuric acid treated acorn waste: Equilibrium and kinetic studies.
OYARO, N., OGENDI, J., MURAGO, E. N. M. & GITONGA, E. 2007. The contents of Pb, Cu, Zn and Cd in meat in nairobi, Kenya.
ÖZCAN, A. S. & ÖZCAN, A. 2004. Adsorption of acid dyes from aqueous solutions onto acid-activated bentonite.
ÖZER, A., ÖZER, D. & EKIZ, H. I. 1999. Application of Freundlich and Langmuir models to multistage purification process to remove heavy metal ions by using Schizomeris leibleinii. *Process Biochemistry,* 34**,** 919-927.
PAGE, M. M. & PAGE, C. L. 2002. Electroremediation of contaminated soils. *Journal of Environmental Engineering,* 128**,** 208-219.
PAOLETTI, E., SCHAUB, M., MATYSSEK, R., WIESER, G., AUGUSTAITIS, A., BASTRUP-BIRK, A. M., BYTNEROWICZ, A., GÜNTHARDT-GOERG, M. S., MÜLLER-STARCK, G. & SERENGIL, Y. 2010. Advances of air pollution science: from forest decline to multiple-stress effects on forest ecosystem services. *Environmental Pollution,* 158**,** 1986-1989.
PARK, B. & SON, Y. 2017. Ultrasonic and mechanical soil washing processes for the removal of heavy metals from soils. *Ultrasonics sonochemistry,* 35**,** 640-645.

PARK, J. H., CHOPPALA, G. K., BOLAN, N. S., CHUNG, J. W. & CHUASAVATHI, T. 2011. Biochar reduces the bioavailability and phytotoxicity of heavy metals. *Plant and Soil,* 348**,** 439.

PARKER, D. R. & PEDLER, J. F. 1997. Reevaluating the free-ion activity model of trace metal availability to higher plants. *Plant and Soil,* 196**,** 223-228.

PATIL, D. S., CHAVAN, S. M. & OUBAGARANADIN, J. U. K. 2016. A review of technologies for manganese removal from wastewaters. *Journal of Environmental Chemical Engineering,* 4**,** 468-487.

PAUL, D. 2017. Research on heavy metal pollution of river Ganga: A review. *Annals of Agrarian Science*.

PAULINO, A. T., MINASSE, F. A. S., GUILHERME, M. R., REIS, A. V., MUNIZ, E. C. & NOZAKI, J. 2006. Novel adsorbent based on silkworm chrysalides for removal of heavy metals from wastewaters. *Journal of colloid and interface science,* 301**,** 479-487.

PAVAN, M. A., BINGHAM, F. T. & PRATT, P. F. 1982. Toxicity of aluminum to coffee in Ultisols and Oxisols amended with CaCO3, MgCO3, and CaSO4· 2H2O. *Soil Science Society of America Journal,* 46**,** 1201-1207.

PEHLIVAN, E., ALTUN, T. & PARLAYICI, Ş. 2012. Modified barley straw as a potential biosorbent for removal of copper ions from aqueous solution. *Food Chemistry,* 135**,** 2229-2234.

PEHLIVAN, E., YANıK, B. H., AHMETLI, G. & PEHLIVAN, M. 2008. Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp. *Bioresource technology,* 99**,** 3520-3527.

PEIJNENBURG, W. & JAGER, T. 2003. Monitoring approaches to assess bioaccessibility and bioavailability of metals: matrix issues. *Ecotoxicology and environmental safety,* 56**,** 63-77.

PELCOVÁ, P., DOČEKALOVÁ, H. & KLECKEROVÁ, A. 2014. Development of the diffusive gradient in thin films technique for the measurement of labile mercury species in waters. *Analytica Chimica Acta,* 819**,** 42-48.

PENG, Q., WANG, M., CUI, Z., HUANG, J., CHEN, C., GUO, L. & LIANG, D. 2017a. Assessment of bioavailability of selenium in different plant-soil systems by diffusive gradients in thin-films (DGT). *Environmental Pollution,* 225**,** 637-643.

PENG, W., LI, H., LIU, Y. & SONG, S. 2016. Comparison of Pb (II) adsorption onto graphene oxide prepared from natural graphites: diagramming the Pb (II) adsorption sites. *Applied Surface Science,* 364**,** 620-627.

PENG, W., LI, H., LIU, Y. & SONG, S. 2017b. A review on heavy metal ions adsorption from water by graphene oxide and its composites. *Journal of Molecular Liquids,* 230**,** 496-504.

PENG, X., YE, L. L., WANG, C. H., ZHOU, H. & SUN, B. 2011. Temperature-and duration-dependent rice straw-derived biochar: Characteristics and its effects on soil properties of an Ultisol in southern China. *Soil and Tillage Research,* 112**,** 159-166.

PÉREZ-MARÍN, A. B., ZAPATA, V. M., ORTUNO, J. F., AGUILAR, M., SÁEZ, J. & LLORÉNS, M. 2007. Removal of cadmium from aqueous solutions by adsorption onto orange waste. *Journal of hazardous materials,* 139**,** 122-131.

PERSAUD, G. & CANTWELL, F. F. 1992. Determination of free magnesium ion concentration in aqueous solution using 8-hydroxyquinoline immobilized on a nonpolar adsorbent. *Analytical Chemistry,* 64**,** 89-94.

PETRUZZELLI, G. Soil contamination and remediation strategies. Current research and future challenge. EGU General Assembly Conference Abstracts, 2012. 7963.

PINO, G. H., DE MESQUITA, L. M. S., TOREM, M. L. & PINTO, G. A. S. 2006a. Biosorption of cadmium by green coconut shell powder. *Minerals Engineering,* 19**,** 380-387.

PINO, G. H., DE MESQUITA, L. M. S., TOREM, M. L. & PINTO, G. A. S. 2006b. Biosorption of heavy metals by powder of green coconut shell. *Separation Science and Technology,* 41**,** 3141-3153.

PLAYLE, R. C. 1998. Modelling metal interactions at fish gills. *Science of the Total Environment,* 219**,** 147-163.

POOTS, V. J. P., MCKAY, G. & HEALY, J. J. 1978. Removal of basic dye from effluent using wood as an adsorbent. *Journal (Water Pollution Control Federation)***,** 926-935.

POPE, C. A., 3RD, BURNETT, R. T., THURSTON, G. D., THUN, M. J., CALLE, E. E., KREWSKI, D. & GODLESKI, J. J. 2004. Cardiovascular mortality and long-term exposure to particulate air pollution: epidemiological evidence of general pathophysiological pathways of disease. *Circulation,* 109**,** 71-77.

PORTER, S. K., SCHECKEL, K. G., IMPELLITTERI, C. A. & RYAN, J. A. 2004. Toxic metals in the environment: thermodynamic considerations for possible immobilization strategies for Pb, Cd, As, and Hg. *Critical Reviews in Environmental Science and Technology,* 34**,** 495-604.

PRASAD, M. N. V. 2003. Phytoremediation of metal-polluted ecosystems: hype for commercialization. *Russian Journal of Plant Physiology,* 50**,** 686-701.

RAHMAN, M., HASAN, N., DAS, A. K., HOSSAIN, T., JAHAN, R., KHATUN, A. & RAHMATULLAH, M. 2011. Effect Of Delonix Regia Leaf Extract On Glucose Tolerance In Glucoseinduced Hyperglycemic Mice. *African Journal of Traditional, Complementary and Alternative Medicines,* 8.

RAO, P. S., REDDY, K. V. N. S., KALYANI, S. & KRISHNAIAH, A. 2007. Comparative sorption of copper and nickel from aqueous solutions by natural neem (Azadirachta indica) sawdust and acid treated sawdust. *Wood Science and Technology,* 41**,** 427-442.

REBELE, F., SURMA, A., KUZNIK, C., BORNKAMM, R. & BREJ, T. 1993. Heavy metal contamination of spontaneous vegetation and soil around the copper smelter" Legnica". *Acta Societatis Botanicorum Poloniae,* 62**,** 53-57.

REDDY, D. H. K., RAMANA, D. K. V., SESHAIAH, K. & REDDY, A. V. R. 2011. Biosorption of Ni (II) from aqueous phase by Moringa oleifera bark, a low cost biosorbent. *Desalination,* 268**,** 150-157.

RENBERG, I., PERSSON, M. W. & EMTERYD, O. 1994. Pre-industrial atmospheric lead contamination detected in Swedish lake sediments. *Nature,* 368**,** 323-326.

RENGE, V. & KHEDKAR, S. 2012. Removal of heavy metals from wastewater using low cost adsorbents: a review. *Scientific Reviews and Chemical Communications,* 2.

RIEUWERTS, J., ASHMORE, M., FARAGO, M. & THORNTON, I. 2006. The influence of soil characteristics on the extractability of Cd, Pb and Zn in upland and moorland soils. *Science of the total Environment,* 366**,** 864-875.

RIEUWERTS, J., THORNTON, I., FARAGO, M. & ASHMORE, M. 1998. Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. *Chemical Speciation & Bioavailability,* 10**,** 61-75.

RØDSAND, T., ACAR, Y. B. & BREEDVELD, G. 1996. Electrokinetic extraction of lead from spiked Norwegian marine clay. *Publikasjon-Norges Geotekniske Institutt,* 195**,** 1518-1535.

ROY, I., MANDAL, J., CHATTERJEE, S. & GUPTA-BHATTACHARYA, S. 2008. Aerobiological investigation and in vitro studies of pollen grains from 2 dominant avenue trees in Kolkata, India.

RUIHUA, L., LIN, Z., TAO, T. & BO, L. 2011. Phosphorus removal performance of acid mine drainage from wastewater. *Journal of hazardous materials,* 190**,** 669-676.

SAEED, A., IQBAL, M. & AKHTAR, M. W. 2005. Removal and recovery of lead (II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). *Journal of hazardous materials,* 117**,** 65-73.

SAEED, A., IQBAL, M. & WAHEED AKHTAR, M. 2002. Application of biowaste materials for the sorption of heavy metals in contaminated aqueous medium. *Pakistan Journal of Scientific and Industrial Research,* 45**,** 206-211.

SAHA, R. & SAHA, B. 2014. Removal of hexavalent chromium from contaminated water by adsorption using mango leaves (Mangifera indica). *Desalination and Water Treatment,* 52**,** 1928-1936.

SAHUQUILLO, A., RIGOL, A. & RAURET, G. 2003. Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments. *TrAC Trends in Analytical Chemistry,* 22**,** 152-159.

SAIFUDDIN, M. & KUMARAN, P. 2005. Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic Journal of Biotechnology,* 8**,** 43-53.

SAKA, C., ŞAHIN, Ö., DEMIR, H. & KAHYAOĞLU, M. 2011. Removal of lead (II) from aqueous solutions using pre-boiled and formaldehyde-treated onion skins as a new adsorbent. *Separation Science and Technology,* 46**,** 507-517.

SAKA, C., ŞAHIN, Ö. & KÜÇÜK, M. M. 2012. Applications on agricultural and forest waste adsorbents for the removal of lead (II) from contaminated waters. *International Journal of Environmental Science and Technology,* 9**,** 379-394.

SAMAKSAMAN, U., PENG, T.-H., KUO, J.-H., LU, C.-H. & WEY, M.-Y. 2016. Thermal treatment of soil co-contaminated with lube oil and heavy metals in a low-temperature two-stage fluidized bed incinerator. *Applied Thermal Engineering,* 93**,** 131-138.

SANDAU, E., SANDAU, P. & PULZ, O. 1996. Heavy metal sorption by microalgae. *Engineering in Life Sciences,* 16**,** 227-235.

SARI, A., MENDIL, D., TUZEN, M. & SOYLAK, M. 2009. Biosorption of palladium (II) from aqueous solution by moss (Racomitrium lanuginosum) biomass: Equilibrium, kinetic and thermodynamic studies. *Journal of hazardous materials,* 162**,** 874-879.

SAUVÉ, S., HENDERSHOT, W. & ALLEN, H. E. 2000. Solid-solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. *Environmental science & technology,* 34**,** 1125-1131.

SAUVÉ, S., MCBRIDE, M. B. & HENDERSHOT, W. H. 1995. Ion-selective electrode measurements of copper (II) activity in contaminated soils. *Archives of Environmental Contamination and Toxicology,* 29**,** 373-379.

SCHINTU, M., MARRAS, B., DURANTE, L., MELONI, P. & CONTU, A. 2010. Macroalgae and DGT as indicators of available trace metals in marine coastal waters near a lead–zinc smelter. *Environmental monitoring and assessment,* 167**,** 653-661.

SEKARA, A., PONIEDZIALEEK, M., CIURA, J. & JEDRSZCZYK, E. 2005. Cadmium and lead accumulation and distribution in the organs of nine crops: implications for phytoremediation. *Polish Journal of Environmental Studies,* 14**,** 509-516.

SEN, T. K., MOHAMMOD, M., MAITRA, S. & DUTTA, B. K. 2010. Removal of cadmium from aqueous solution using castor seed hull: a kinetic and equilibrium study. *CLEAN–Soil, Air, Water,* 38**,** 850-858.

SENTHIL KUMAR, P., RAMALINGAM, S., ABHINAYA, R. V., KIRUPHA, S. D., MURUGESAN, A. & SIVANESAN, S. 2012. Adsorption of metal ions onto the chemically modified agricultural waste. *CLEAN–Soil, Air, Water,* 40**,** 188-197.

SENTHILKUMAR, P., RAMALINGAM, S., SATHYASELVABALA, V., KIRUPHA, S. D. & SIVANESAN, S. 2011. Removal of copper (II) ions from aqueous solution by adsorption using cashew nut shell. *Desalination,* 266**,** 63-71.

SHABUDEEN, S. P. S., DANIEL, S. & INDHUMATHI, P. 2013. Utilising the pods of Delonix regia activated carbon for the removal of mercury (II) by adsorption technique. *International Journal of Research in Chemistry and Environment,* 3**,** 60-65.

SHAHID, M., AUSTRUY, A., ECHEVARRIA, G., ARSHAD, M., SANAULLAH, M., ASLAM, M., NADEEM, M., NASIM, W. & DUMAT, C. 2014a. EDTA-enhanced phytoremediation of

heavy metals: a review. *Soil and Sediment Contamination: An International Journal,* 23**,** 389-416.

SHAHID, M., POURRUT, B., DUMAT, C., NADEEM, M., ASLAM, M. & PINELLI, E. 2014b. Heavy-metal-induced reactive oxygen species: phytotoxicity and physicochemical changes in plants. *Reviews of Environmental Contamination and Toxicology Volume 232.* Springer.

SHAHID, M., XIONG, T., MASOOD, N., LEVEQUE, T., QUENEA, K., AUSTRUY, A., FOUCAULT, Y. & DUMAT, C. 2014c. Influence of plant species and phosphorus amendments on metal speciation and bioavailability in a smelter impacted soil: a case study of food-chain contamination. *Journal of soils and sediments,* 14**,** 655-665.

SHARMA, S. & IMRAN, A. 2011. Adsorption of Rhodamine B dye from aqueous solution onto acid activated mango (Magnifera indica) leaf powder: equilibrium, kinetic and thermodynamic studies. *Journal of Toxicology and Environmental Health Sciences,* 3**,** 286-297.

SHAW, J. 1989. *Heavy metal tolerance in plants: evolutionary aspects*, CRC Press.

SHENG, G., YANG, Y., HUANG, M. & YANG, K. 2005. Influence of pH on pesticide sorption by soil containing wheat residue-derived char. *Environmental Pollution,* 134**,** 457-463.

SHUKLA, S. R. & PAI, R. S. 2005. Adsorption of Cu (II), Ni (II) and Zn (II) on modified jute fibres. *Bioresource technology,* 96**,** 1430-1438.

SIAL, R. A., CHAUDHARY, M. F., ABBAS, S. T., LATIF, M. I. & KHAN, A. G. 2006. Quality of effluents from Hattar industrial estate. *Journal of Zhejiang University SCIENCE B,* 7**,** 974-980.

SLAVEYKOVA, V. I. & WILKINSON, K. J. 2002. Physicochemical aspects of lead bioaccumulation by Chlorella vulgaris. *Environmental science & technology,* 36**,** 969-975.

SMIČIKLAS, I., SMILJANIĆ, S., PERIĆ-GRUJIĆ, A., ŠLJIVIĆ-IVANOVIĆ, M., MITRIĆ, M. & ANTONOVIĆ, D. 2014. Effect of acid treatment on red mud properties with implications on Ni (II) sorption and stability. *Chemical Engineering Journal,* 242**,** 27-35.

SMITH, L. A. 1995. *Remedial options for metals-contaminated sites*, Lewis Publ.

SOARES, M. A. R., QUINA, M. J. & QUINTA-FERREIRA, R. M. 2015. Immobilisation of lead and zinc in contaminated soil using compost derived from industrial eggshell. *Journal of environmental management,* 164**,** 137-145.

SONG, Z., DONG, L., SHAN, B. & TANG, W. 2018. Assessment of potential bioavailability of heavy metals in the sediments of land-freshwater interfaces by diffusive gradients in thin films. *Chemosphere,* 191**,** 218-225.

SÖRME, L. & LAGERKVIST, R. 2002. Sources of heavy metals in urban wastewater in Stockholm. *Science of the Total Environment,* 298**,** 131-145.

STEGMANN, R., BRUNNER, G., CALMANO, W. & MATZ, G. 2013. *Treatment of contaminated soil: fundamentals, analysis, applications*, Springer Science & Business Media.

SUDHA, R., SRINIVASAN, K. & PREMKUMAR, P. 2015. Removal of nickel (II) from aqueous solution using Citrus Limettioides peel and seed carbon. *Ecotoxicology and environmental safety,* 117**,** 115-123.

SUGUMARAN, P., SUSAN, V. P., RAVICHANDRAN, P. & SESHADRI, S. 2012. Production and characterization of activated carbon from banana empty fruit bunch and Delonix regia fruit pod. *Journal of Sustainable Energy & Environment,* 3**,** 125-132.

TAHA, G., ARIFIEN, A. & EL-NAHAS, S. 2011. Removal efficiency of potato peels as a new biosorbent material for uptake of Pb (II) Cd (II) and Zn (II) from their aqueous solutions. *The Journal of Solid Waste Technology and Management,* 37**,** 128-140.

TANG, J., ZHU, W., KOOKANA, R. & KATAYAMA, A. 2013. Characteristics of biochar and its application in remediation of contaminated soil. *Journal of bioscience and bioengineering,* 116**,** 653-659.

TEE, T. W. & KHAN, A. R. M. 1988. Removal of lead, cadmium and zinc by waste tea leaves. *Environmental Technology,* 9**,** 1223-1232.
TEMMINGHOFF, E. J. M., PLETTE, A. C. C., VAN ECK, R. & VAN RIEMSDIJK, W. H. 2000. Determination of the chemical speciation of trace metals in aqueous systems by the Wageningen Donnan Membrane Technique. *Analytica Chimica Acta,* 417**,** 149-157.
TEMPLETON, D. M., ARIESE, F., CORNELIS, R., DANIELSSON, L.-G., MUNTAU, H., VAN LEEUWEN, H. P. & LOBINSKI, R. 2000. Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches (IUPAC Recommendations 2000). *Pure and applied chemistry,* 72**,** 1453-1470.
THOMAS, G. 1996. Soil pH and soil acidity. *Methods of Soil Analysis Part 3—Chemical Methods***,** 475-490.
TIAN, Y., WANG, X., LUO, J., YU, H. & ZHANG, H. 2008. Evaluation of holistic approaches to predicting the concentrations of metals in field-cultivated rice. *Environmental science & technology,* 42**,** 7649-7654.
TIWARI, D., MISHRA, S. P., MISHRA, M. & DUBEY, R. 1999. Biosorptive behaviour of Mango (Mangifera indica) and Neem (Azadirachta indica) bark for Hg 2+, Cr 3+ and Cd 2+ toxic ions from aqueous solutions: a radiotracer study. *Applied Radiation and Isotopes,* 50**,** 631-642.
TRIPATHI, A. & RANJAN, M. R. 2015. Heavy metal removal from wastewater using low cost adsorbents. *J. Biorem. Biodegrad.,* 6**,** 315.
TRIPLETT KINGSTON, J. L., DAHLEN, P. R. & JOHNSON, P. C. 2012. Assessment of groundwater quality improvements and mass discharge reductions at five in situ electrical resistance heating remediation sites. *Groundwater Monitoring & Remediation,* 32**,** 41-51.
TYAGI, I., GUPTA, V., SADEGH, H., GHOSHEKANDI, R. & MAKHLOUF, A. S. H. 2017. Nanoparticles as adsorbent; a positive approach for removal of noxious metal ions: a review. *Science Technology and Development,* 34**,** 195-214.
UCHIMIYA, M., KLASSON, K. T., WARTELLE, L. H. & LIMA, I. M. 2011. Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorption isotherms and the release of cations. *Chemosphere,* 82**,** 1431-1437.
UCHIMIYA, M., LIMA, I. M., KLASSON, K. T. & WARTELLE, L. H. 2010. Contaminant immobilization and nutrient release by biochar soil amendment: Roles of natural organic matter. *Chemosphere,* 80**,** 935-940.
ULLAH, R., MALIK, R. N. & QADIR, A. 2009. Assessment of groundwater contamination in an industrial city, Sialkot, Pakistan. *African Journal of Environmental Science and Technology,* 3.
USMAN, M., FAURE, P., RUBY, C. & HANNA, K. 2012. Remediation of PAH-contaminated soils by magnetite catalyzed Fenton-like oxidation. *Applied Catalysis B: Environmental,* 117**,** 10-17.
UTOMO, W. H., KUSUMA, Z. & NUGROHO, W. H. 2011. Soil fertility status, nutrient uptake, and maize (Zea mays L.) yield following biochar and cattle manure application on sandy soils of Lombok, Indonesia. *Journal of Tropical Agriculture,* 49**,** 47-52.
VAN AKEN, B. 2009. Transgenic plants for enhanced phytoremediation of toxic explosives. *Current Opinion in Biotechnology,* 20**,** 231-236.
VANDEGRIFT, G. F., REED, D. T. & TASKER, I. R. 1992. *Environmental remediation: removing organic and metal ion pollutants*, ACS Publications.
VANGRONSVELD, J. 1998. *Metal-contaminated soils: in-situ inactivation and phytorestoration*, Springer.
VANGRONSVELD, J., HERZIG, R., WEYENS, N., BOULET, J., ADRIAENSEN, K., RUTTENS, A., THEWYS, T., VASSILEV, A., MEERS, E. & NEHNEVAJOVA, E. 2009. Phytoremediation of

contaminated soils and groundwater: lessons from the field. *Environmental Science and Pollution Research,* 16**,** 765-794.
VARGAS, A. M. M., CAZETTA, A. L., KUNITA, M. H., SILVA, T. L. & ALMEIDA, V. C. 2011. Adsorption of methylene blue on activated carbon produced from flamboyant pods (Delonix regia): Study of adsorption isotherms and kinetic models. *Chemical Engineering Journal,* 168**,** 722-730.
VASEEM, H., SINGH, V. K. & SINGH, M. P. 2017. Heavy metal pollution due to coal washery effluent and its decontamination using a macrofungus, Pleurotus ostreatus. *Ecotoxicology and environmental safety,* 145**,** 42-49.
VERGILI, I., GÖNDER, Z. B., KAYA, Y., GÜRDAĞ, G. & ÇAVUŞ, S. 2017. Sorption of Pb (II) from battery industry wastewater using a weak acid cation exchange resin. *Process Safety and Environmental Protection,* 107**,** 498-507.
VIMALA, R. & DAS, N. 2009. Biosorption of cadmium (II) and lead (II) from aqueous solutions using mushrooms: a comparative study. *Journal of hazardous materials,* 168**,** 376-382.
VIOLANTE, A., COZZOLINO, V., PERELOMOV, L., CAPORALE, A. & PIGNA, M. 2010. Mobility and bioavailability of heavy metals and metalloids in soil environments. *Journal of soil science and plant nutrition,* 10**,** 268-292.
VIRKUTYTE, J., SILLANPÄÄ, M. & LATOSTENMAA, P. 2002. Electrokinetic soil remediation—critical overview. *Science of the Total Environment,* 289**,** 97-121.
VOLESKY, B. 1990. *Biosorption of heavy metals*, CRC press.
VOLESKY, B. & HOLAN, Z. R. 1995. Biosorption of heavy metals. *Biotechnology progress,* 11**,** 235-250.
VUNAIN, E., MISHRA, A. K. & MAMBA, B. B. 2016. Dendrimers, mesoporous silicas and chitosan-based nanosorbents for the removal of heavy-metal ions: A review. *International journal of biological macromolecules,* 86**,** 570-586.
WALKER, D. J., CLEMENTE, R. & BERNAL, M. P. 2004. Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of Chenopodium album L. in a soil contaminated by pyritic mine waste. *Chemosphere,* 57**,** 215-224.
WANG, H., YUAN, X., WU, Y., HUANG, H., ZENG, G., LIU, Y., WANG, X., LIN, N. & QI, Y. 2013a. Adsorption characteristics and behaviors of graphene oxide for Zn (II) removal from aqueous solution. *Applied Surface Science,* 279**,** 432-440.
WANG, P., ZHANG, Q., LI, Y., MATSIKO, J., ZHANG, Y. & JIANG, G. 2017. Airborne persistent toxic substances (PTSs) in China: occurrence and its implication associated with air pollution. *Environmental Science: Processes & Impacts,* 19**,** 983-999.
WANG, S.-L., XU, X.-R., SUN, Y.-X., LIU, J.-L. & LI, H.-B. 2013b. Heavy metal pollution in coastal areas of South China: a review. *Marine pollution bulletin,* 76**,** 7-15.
WATTS, J. 2009. *Lead poisoning cases spark riots in China*.
WEBER, T. W. & CHAKRAVORTI, R. K. 1974. Pore and solid diffusion models for fixed-bed adsorbers. *AIChE Journal,* 20**,** 228-238.
WEGGLER, K., MCLAUGHLIN, M. J. & GRAHAM, R. D. 2004. Effect of chloride in soil solution on the plant availability of biosolid-borne cadmium. *Journal of environmental quality,* 33**,** 496-504.
WEI, B. & YANG, L. 2010. A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. *Microchemical Journal,* 94**,** 99-107.
WEI, M., CHEN, J. & WANG, X. 2016. Removal of arsenic and cadmium with sequential soil washing techniques using Na 2 EDTA, oxalic and phosphoric acid: optimization conditions, removal effectiveness and ecological risks. *Chemosphere,* 156**,** 252-261.
WILDE, E. W. & BENEMANN, J. R. 1993. Bioremoval of heavy metals by the use of microalgae. *Biotechnology Advances,* 11**,** 781-812.
WINGATE, J. R., SNEATH, H., HUTCHINGS, T. & DE LEIJ, F. 2008. Potential of non-activated charcoals for land remediation. *University of Surrey*.

WITEK-KROWIAK, A. & REDDY, D. H. K. 2013. Removal of microelemental Cr (III) and Cu (II) by using soybean meal waste–unusual isotherms and insights of binding mechanism. *Bioresource technology,* 127**,** 350-357.

WITEK-KROWIAK, A., SZAFRAN, R. G. & MODELSKI, S. 2011. Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent. *Desalination,* 265**,** 126-134.

WUANA, R. A. & OKIEIMEN, F. E. 2011. Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. *Isrn Ecology,* 2011.

XIAN, X. & SHOKOHIFARD, G. I. 1989. Effect of pH on chemical forms and plant availability of cadmium, zinc, and lead in polluted soils. *Water, air, and soil pollution,* 45**,** 265-273.

XUE, Y., HOU, H. & ZHU, S. 2009. Competitive adsorption of copper (II), cadmium (II), lead (II) and zinc (II) onto basic oxygen furnace slag. *Journal of hazardous materials,* 162**,** 391-401.

YAN, L., YIN, H., ZHANG, S., LENG, F., NAN, W. & LI, H. 2010. Biosorption of inorganic and organic arsenic from aqueous solution by Acidithiobacillus ferrooxidans BY-3. *Journal of hazardous materials,* 178**,** 209-217.

YANG, S., LI, J., SHAO, D., HU, J. & WANG, X. 2009. Adsorption of Ni (II) on oxidized multi-walled carbon nanotubes: effect of contact time, pH, foreign ions and PAA. *Journal of hazardous materials,* 166**,** 109-116.

YAO, Y., SUN, Q., WANG, C., WANG, P.-F. & DING, S.-M. 2017. Evaluation of organic amendment on the effect of cadmium bioavailability in contaminated soils using the DGT technique and traditional methods. *Environmental Science and Pollution Research,* 24**,** 7959-7968.

YOUNG, S. D., ZHANG, H., TYE, A. M., MAXTED, A., THUMS, C. & THORNTON, I. 2005. Characterizing the availability of metals in contaminated soils. I. The solid phase: sequential extraction and isotopic dilution. *Soil Use and Management,* 21**,** 450-458.

ZAFAR, M. N., NADEEM, R. & HANIF, M. A. 2007. Biosorption of nickel from protonated rice bran. *Journal of hazardous materials,* 143**,** 478-485.

ZERAATKAR, A. K., AHMADZADEH, H., TALEBI, A. F., MOHEIMANI, N. R. & MCHENRY, M. P. 2016. Potential use of algae for heavy metal bioremediation, a critical review. *Journal of environmental management,* 181**,** 817-831.

ZHANG, H. & DAVISON, W. 1995. Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solution. *Analytical Chemistry,* 67**,** 3391-3400.

ZHANG, H. & DAVISON, W. 1999. Diffusional characteristics of hydrogels used in DGT and DET techniques. *Analytica Chimica Acta,* 398**,** 329-340.

ZHANG, H., DAVISON, W., KNIGHT, B. & MCGRATH, S. 1998. In situ measurements of solution concentrations and fluxes of trace metals in soils using DGT. *Environmental science & technology,* 32**,** 704-710.

ZHANG, H., DAVISON, W., MORTIMER, R. J. G., KROM, M. D., HAYES, P. J. & DAVIES, I. M. 2002. Localised remobilization of metals in a marine sediment. *Science of the Total Environment,* 296**,** 175-187.

ZHANG, H., DAVISON, W., TYE, A. M., CROUT, N. M. J. & YOUNG, S. D. 2006. Kinetics of zinc and cadmium release in freshly contaminated soils. *Environmental toxicology and chemistry,* 25**,** 664-670.

ZHANG, H., LOMBI, E., SMOLDERS, E. & MCGRATH, S. 2004a. Kinetics of Zn release in soils and prediction of Zn concentration in plants using diffusive gradients in thin films. *Environmental science & technology,* 38**,** 3608-3613.

ZHANG, H., LOMBI, E., SMOLDERS, E. & MCGRATH, S. 2004b. Zn availability in field contaminated and spiked soils. *Environ.Sci.Technol,* 38**,** 3608-3613.

ZHANG, H. & YOUNG, S. D. 2005. Characterizing the availability of metals in contaminated soils. II. *Soil Use and Management,* 21**,** 459-467.

ZHANG, H., ZHAO, F.-J., SUN, B., DAVISON, W. & MCGRATH, S. P. 2001. A new method to measure effective soil solution concentration predicts copper availability to plants. *Environmental science & technology,* 35**,** 2602-2607.

ZHANG, X., WANG, H., HE, L., LU, K., SARMAH, A., LI, J., BOLAN, N. S., PEI, J. & HUANG, H. 2013. Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. *Environmental Science and Pollution Research,* 20**,** 8472-8483.

ZHANG, X. & WANG, X. 2015. Adsorption and desorption of nickel (II) ions from aqueous solution by a lignocellulose/montmorillonite nanocomposite. *PloS one,* 10**,** e0117077.

ZHENG, C. & WANG, P. P. 2002. A field demonstration of the simulation optimization approach for remediation system design. *Groundwater,* 40**,** 258-266.

ZHOU, G., LUO, J., LIU, C., CHU, L., MA, J., TANG, Y., ZENG, Z. & LUO, S. 2016. A highly efficient polyampholyte hydrogel sorbent based fixed-bed process for heavy metal removal in actual industrial effluent. *Water research,* 89**,** 151-160.

ZHU, L., DING, W., FENG, L.-J., KONG, Y., XU, J. & XU, X.-Y. 2012. Isolation of aerobic denitrifiers and characterization for their potential application in the bioremediation of oligotrophic ecosystem. *Bioresource technology,* 108**,** 1-7.